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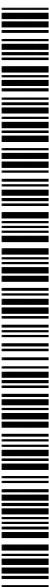
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(54) Title: HYDROGEN CATALYSIS

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(57) Abstract: A catalytic reaction of atomic hydrogen is provided which produces a more stable or lower energy atomic hydrogen atom than uncatalyzed atomic hydrogen. The catalyzed lower energy hydrogen atom may serve as a reactant of a disproportionation reaction whereby it which accepts energy from a second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes a nonradiative electronic transition to a higher energy level while the second undergoes a transition to a lower energy level. The catalytic reaction and disproportionation reaction of lower energy atomic hydrogen may produce light, plasma, power, and novel hydrogen compounds. The light, plasma, power and compound source comprises a cell for the catalysis of atomic hydrogen and disproportionation reactions of lower energy atomic hydrogen to form novel hydrogen species and compositions of matter comprising hydrogen that is more stable or lower energy than uncatalyzed hydrogen. The compounds comprise at least one neutral, positive, or negative hydrogen species having a binding energy greater than its corresponding ordinary hydrogen species, or greater than any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed.

**METHOD FOR FORMING A SILICIDE GATE STACK
FOR USE IN A SELF-ALIGNED CONTACT ETCH**

Field of the Invention

5 The present invention relates to the field of semiconductor integrated circuits and, in particular, to a silicide structure capable of use in a self-aligned contact (SAC) etch.

Background of the Invention

10 Semiconductor integrated circuits with high device density require the patterning of closely spaced features including, for example, active areas, insulation structures, gates for field effect transistors, narrow conductors and interconnection lines, among others.

15 The formation of such polysilicon, metal, or insulation structures typically requires definition of the features in structures in a layer of photoresist, on a layer of polysilicon or insulator, by exposure of the photoresist with light passing through a reticle or photomask containing the desired pattern. After exposure and development of the photoresist, the underlying layer of the
20 substrate is etched using the patterned photoresist as a template. The masking material protects designated areas of the substrate from the etch process. Subsequent processing steps are determined according to the type of device to be fabricated.

25 During these processing steps, problems with the misalignment of successive mask patterns relative to one another often occur. For example, deposited contacts might not line up correctly inside contact holes, source and drain regions might not line up perfectly relative to the gate region, and

connections that must be physically close, but require electrical isolation from one another, might develop short circuits.

In an effort to reduce the misalignment problems of successive mask patterns, different techniques have been introduced into the IC fabrication.

One of them is the salicide (self-aligned silicide) process, where a layer of polysilicon is first patterned so that a metal deposited over the wafer could then be annealed to form a metal silicide only in the area with exposed polysilicon.

The salicide process relies on the fact that certain metals, such as cobalt or titanium, react under high temperatures with silicon to form conductive silicides, but do not react with silicon oxide. The unreacted metal is subsequently etched away, leaving the silicide self-aligned to the polysilicon, and automatically aligned to gate and source/drain regions. The metal in the silicide confers a lower resistance to the gate stack line, which, in turn, increases the speed of the devices.

Another technique commonly used to align a contact with an active area is the self-aligned contact (SAC) process, which involves an anisotropic etch to form a via or a contact hole that passes through the oxide layer down to the source/drain surface. The contact hole may not be perfectly aligned with the source and drain because spacers shield the vertical walls of the gate. Spacers, however, are very thin at the top of a gate and the etch-through of the top spacers during the SAC cannot be avoided. Accordingly, the polysilicon gate is typically covered with a silicon nitride or TEOS layer to form a dielectric cap material covering the gate to protect it during a SAC etch. During the formation of the contact hole in a SAC etch, a certain amount of the nitride material is removed but a sufficient amount remains so that when conductive material is deposited in the contact hole it does not short to the gate.

Until recently, logic and memory devices were packed separately, on different chips. The salicide process was used mainly for logic circuits because it made possible higher circuit performance. Similarly, the SAC process was employed primarily for memory circuits because it allowed the reduction of the cell size of the memory unit while achieving correct contact/active area alignment. As long as the logic and memory units were on separate chips, each of the two processes could be used separately without any effect on each other or implication on the overall circuit performance.

Recently, however, advanced semiconductor chips manufactured in the industry are composed of both logic and memory devices. Thus, for performance and cost reasons, current IC integration dictates the placing of logic and memory circuit on the same chip. Further, as the feature sizes continue to decrease, it may become necessary for memory chips to use low resistance gate materials, even if the memory chips are not embedded with logic devices on the same chip.

Efforts in the semiconductor industry attempting to incorporate both logic and memory applications on a single semiconductor chip have been increasing. Nevertheless, while there are many references to both the salicide and the SAC processes, only few address their actual integration.

For example, U.S. Patent No. 5,863,820 to Huang describes a process for the integration of SAC and salicide processes on one chip, in which the polysilicon gate pedestals are formed first, those in the memory area having a silicon nitride on top. Subsequently, spacers are grown on the vertical walls of the gate pedestals and source and drain regions are formed. The gate pedestals on the memory side are then given a protective coating of oxide (RPO). This protective coating allows the salicide process to be selectively applied only to the

ogic side. Once the logic side is protected, a SAC process is applied to the memory side.

The methods developed by the prior art, however, do not specifically address the problems imposed by the actual simultaneous integration of the salicide and SAC processes on the same area of the chip. For example, when a SAC process is integrated with a salicide process, further adjustments and changes are required in the etch rate, selectivity, and profile control, to name just few of them. In particular, etch selectivity is a critical issue because the current salicide gate stacks are formed without a cap layer over the top of the gate. As described above, a SAC etch process is used to allow larger contacts to be patterned without shorting the contact to the gate by etching the contact selective to a cap material formed over the gate. Thus, although metal silicides confer low resistance to gate stacks, the current gate stacks cannot undergo subsequent SAC processes because the metal silicides formed by a salicide process lack a suitable cap material.

Accordingly, there is a need for an improved method by which the SAC and the salicide processes can be used together on one chip. That is, what is needed is a silicide gate structure that can be subsequently etched under a SAC method.

Summary of the Invention

The present invention provides a method for forming a silicide gate stack that can subsequently undergo a SAC etch. The present method leaves a layer of cap material on top of the silicide gate, which is sufficiently thick to protect the gate during the SAC etch. The deposited cap material is suitable for

ubsequent SAC processes used in contact definition at sub-0.5 micron dimensions.

Additional advantages of the present invention will be more apparent from the detailed description and accompanying drawings, which illustrate preferred embodiments of the invention.

Brief Description of the Drawings

Figure 1 is a schematic cross-sectional view of a portion of a conventional memory DRAM device just prior to the formation of a self-aligned contact etch.

Figure 2 is a schematic cross-sectional view of the Figure 1 device at the beginning of a self-aligned contact etch conducted in accordance with a method of the prior art.

Figure 3 is a schematic cross-sectional view of the Figure 1 device at a subsequent step to that in Figure 2.

Figures 4 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed in accordance with a method of the present invention.

Figure 5 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 4.

Figure 6 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 5.

5 Figure 7 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 6.

10 Figure 8 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 7.

15 Figure 9 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 8.

20 Figure 10 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 9.

Figure 11 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 10.

25 Figure 12 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 11.

Figure 13 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure is formed at a stage subsequent to that shown in Figure 12.

5 Figure 14 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure undergoes a self-aligned contact etch in accordance with a method of the present invention.

10 Figure 15 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure undergoes a self-aligned contact etch at a stage subsequent to that shown in Figure 14.

15 Figure 16 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure undergoes a self-aligned contact etch at a stage subsequent to that shown in Figure 15.

Figure 17 is a schematic cross sectional views of a substrate on which a silicide cobalt gate stack structure undergoes a self-aligned contact etch at a stage subsequent to that shown in Figure 16.

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Detailed Description of the Preferred Embodiments

In the following detailed description, reference is made to various specific embodiments in which the invention may be practiced. These 25 embodiments are described with sufficient detail to enable those skilled in the art to practice the invention, and it is to be understood that other embodiments may be employed, and that structural, logical, and electrical changes may be made.

The terms “wafer” or “substrate” used in the following description may include any semiconductor-based structure that has an exposed silicon surface. Wafer and structure must be understood to include silicon-on insulator (SOI), silicon-on sapphire (SOS), doped and undoped semiconductors, epitaxial layers of silicon supported by a base semiconductor foundation, and other semiconductor structures. The semiconductor need not be silicon-based. The semiconductor could be silicon-germanium, germanium, or gallium arsenide. When reference is made to a wafer or substrate in the following description, previous process steps may have been utilized to form regions or junctions in the base semiconductor or foundation.

The term “silicon dielectric” is used to indicate a silicon-based dielectric material such as silicon nitride or other silicon-based dielectrics with similar chemical characteristics, such as silicon oxide, silicon oxynitride, silicon oxime, and ONO (oxide-nitride-oxide) materials. The following detailed description is, therefore, not to be taken in a limiting sense, and the scope of the present invention is defined by the appended claims.

The present invention provides a method for forming a silicide gate stack that can subsequently undergo a SAC etch. The present method leaves a layer of cap material on top of the silicide gate. The deposited cap material is suitable for subsequent SAC processes used in contact definition at submicron dimensions.

To illustrate this, Figure 1 depicts a conventional memory cell construction for a DRAM at an intermediate stage of the fabrication, in which a representative substrate is etched according to a conventional SAC etch process. A pair of memory cells having respective access transistors are formed within a substrate 12. The wells and transistors are surrounded by a field oxide region

4 that provides isolation. N-type active regions 16 are provided in a doped p-type well 13 of substrate 12 (for NMOS transistors) and the pair of access transistors have respective gate stacks 30.

5 An insulating layer 24 of, for example, BPSG has been applied over the substrate and transistor structures and a mask layer 26 having openings for etching the insulating layer to form contact openings to active regions 16 are also shown. A self-aligned contact etch of the insulating layer 24, to provide contact openings down to the active regions 16, is performed next.

10 A conventional SAC etch process is illustrated in Figures 2-3. These figures show a middle portion of the Figure 1 structure. The Figure 2 structure includes a substrate 12 having a p-well 13, which is typically doped to a predetermined conductivity, e.g. p-type or n-type depending on whether 15 NMOS or PMOS transistors will be formed therein. The structure further includes field oxide regions 14 (not shown), conventional doped active areas 16, and a pair of gate stacks 30, all formed according to well-known semiconductor processing techniques. The gate stacks 30 include an oxide layer 18, a conductive layer 20, such as polysilicon, nitride spacers 32 and a nitride cap 22.

20 Above the gate oxide region, the polysilicon gates, and the protective nitride regions, an insulating layer 24 is disposed. Insulating layer 24 could be, for example, borophosphosilicate glass (BPSG), borosilicate glass (BSG), or phosphosilicate glass (PSG).

25 To create a contact opening 40 (Figure 3) into semiconductor substrate 10 through oxide layer 24, a photoresist material 26 is deposited and patterned using conventional photolithography steps. After patterning, an initial opening 27 (Figure 2) is created in photoresist layer 26 to facilitate

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subsequent oxide etching. The structure of Figure 2 is then etched and, as shown in Figure 3, a contact opening 40 is formed through oxide layer 24. The contact opening 40 of Figure 2 is etched so that contact opening 40 contacts a source or drain region 16 of substrate 12.

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In a self-aligned contact technique it is desirable that the contact opening, such as contact opening 40 of Figure 3, be etched without serious damage to the insulating nitride regions overlying the polysilicon gates. That is, the contact opening must be etched with an oxide etch process that has a high oxide-to-nitride selectivity. This is impractical, however, when refractory metal silicide layers are employed for the gate stacks formation as part of the integration of the SAC and salicide processes. As described in the background section, the salicide gate stacks do not have a dielectric cap to allow them to undergo SAC etch processes. The present invention addresses this problem by providing the salicide gate stack with a layer of cap material overlying the gate, which is sufficient to protect the gate stack during the SAC etch. The cap dielectric material further allows the use of both the salicide and SAC processes in semiconductor device fabrication.

20

One embodiment of the present invention fabricated according to the process of the present invention is illustrated in Figures 4-13. This embodiment is a multi-layer structure having a dielectric cap material on top of the silicide gate stack in accordance with the present invention. The resulting multi-layer structure depicted in Figure 13 can be subsequently used in a self-aligned contact etch process.

25

As shown in Figure 4, a gate stack formation according to the present invention begins with the deposition of a TEOS layer 28 on silicon layer 12.

TEOS layer 28 is needed primarily as a barrier to prevent materials that will be applied at subsequent processing steps from penetrating silicon layer 12.

Next, sacrificial oxide layer 24 is deposited over TEOS layer 28 of substrate 12. The oxide layer 24 may consist of substantially undoped silicon dioxide or doped silicon oxide. The undoped silicon dioxide can be formed thermally, by plasma enhanced chemical vapor deposition (PECVD), by low pressure chemical vapor deposition (LPCVD), by a conventional TEOS precursor deposition that is preferably rich in carbon or hydrogen, or by a precursor of gaseous silane (SiH_4) with oxygen.

When doped silicon oxide is used, it is preferable that silicon oxide layer 24 be substantially composed of borophosphosilicate glass (BPSG), borosilicate glass (BSG), or phosphosilicate glass (PSG). It is even more preferable that doped silicon dioxide region 24 be composed of silicon dioxide having doping of about 3% or more for boron and about 3% or more for phosphorus.

According to a preferred embodiment of the present invention, and as shown in Figure 4, the oxide layer 24 is doped and formed of BPSG with a TEOS underlying layer 28, at a temperature between about 400C° to 800C°, to a thickness between about 3000Å to 10000Å.

Referring now to Figure 5, the BPSG oxide layer 24 and the underlying TEOS layer 28 of substrate 12 are etched out by a directional etching process such as reactive ion etch (RIE). The mask 25 (Figure 4) delineates regions 50a and 50b where the gates will be formed during subsequent steps. After the openings where the gates will be later formed are etched, mask 25 is removed.

At the end of the etch process described above, the exposed silicon surfaces of silicon layer 12 are further cleaned so that any damaged surface layers are removed. The damaged silicon surfaces are shown in Figure 5 as regions 52.

5 At this step, a soft and/or a wet etch is employed to clean out the damaged silicon surfaces 52. The etch employed to clean out the damaged silicon surfaces could be any soft etch, such as downstream plasma processing using NF₃ as an etchant.

10 Referring now to Figure 6, gate oxide layers 54 are grown on the newly cleaned silicon surfaces, in openings 50a and 50b. It is important to note that the gate oxide layers 54 are not deposited but rather grown up and down, mostly into the silicon layer 12. Deposited oxide layers have a higher impurity content and therefore are undesirable since the impurities may easily affect the 15 gate performance. As such, thin gate oxide layers 54 are thermally grown in an oxygen-steam ambient, at a temperature between about 750C° to 1000C°, to a thickness between about 30Å to 150Å.

20 As illustrated in Figures 7-8, a polysilicon layer (55 in Figure 7) (56 in Figure 8) is deposited over the gate oxide layers 54 via LPCVD procedures, at a temperature between about 300C° to 700C°. The newly deposited polysilicon layer is subsequently etched selective to the sacrificial oxide BPSG layer 24, so that the remaining polysilicon layers 56 of Figure 8 are formed to a thickness between about 500Å to 1500Å. This thickness must be sufficient for 25 the reaction with the silicide metal, deposited in a subsequent step shown in Figure 9, and for the gate itself.

Referring now to Figures 9-10, a layer of metal capable of forming a silicide (57 in Figure 9) (58 in Figure 10) is deposited over the entire substrate

.2 to a thickness between 200Å to 500Å. A preferred method for depositing the refractory metal is sputtering (RF or DC) but other similar methods such as CVD can be used. Preferably, the refractory metal is substantially composed of cobalt because of its lowered resistance and low resistivity as a silicide.

5 However, refractory metal silicide may comprise any refractory metal, including but not limited to, titanium, tungsten, tantalum, molybdenum, and platinum.

Subsequent to the cobalt deposition, substrate 12 undergoes a rapid thermal anneal (RTA), using conventional furnace procedures, typically at about 10 10 to 60 seconds, in an RTA apparatus, using a N₂ ambient, at about 800°C to 850°C, so that the deposited cobalt in direct contact with the polysilicon layers 56 is converted to its silicide. As shown in Figure 10, the silicide regions 58 form conductive regions on top of polysilicon gates 56.

15 At this point, a selective etchant, such as ammonium hydroxide and hydrogen peroxide in water, may be used to remove all unreacted cobalt (not shown), that is all cobalt that was in contact with the silicon oxide 24 rather than with the polysilicon 56.

20 Referring now to Figure 11, a cap material is deposited over substrate 10 and the substrate top surface is planarized by, for example, a CMP process, so that cap regions 60 are formed over silicide regions 58. The cap material may be formed of silicon dielectrics, such as silicon nitride or silicon oxide. Silicon nitride (Si₃N₄) ("nitride") is preferred, however, because of its unique protective qualities such as moisture resistance, hardness, high dielectric strength, and resistance to oxidation. TEOS or silicon carbides may be used also.

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Preferably, the cap regions 60 are deposited via PECVD procedures, at a temperature between about 300°C to 600°C, to a thickness between about 1000Å to 2000Å. After deposition, the silicon dielectric forming the cap regions 60 is chemically metal polished (CMP), so that any silicon nitride be removed from the BPSG oxide layer 24, leaving the silicon nitride material only over the silicide regions 58, as shown in Figure 11.

In a subsequent step, the BPSG oxide layer 24 and the TEOS layer 28 are selectively etched to the gate stacks that have the newly-formed nitride caps 60. Figure 12 illustrates substrate 10 after the etch of BPSG oxide layer 24 selective to nitride regions 60 and TEOS layer 28. Similarly, Figure 13 illustrates substrate 10 after the etch of TEOS layer. The BPSG oxide layer and the TEOS layer 28 may also both be etched away together.

The etching of the BPSG and TEOS layers may be achieved by wet etching processes or dry etching processes. Dry etching processes are typically used since it allows the simultaneous etching of both BPSG and TEOS layers selective to the nitride caps on top of the gate stacks. This way, the etching of the BPSG allows also all TEOS to be taken off in the same process chamber, only by changing the etch chemistry slightly. For example, the BPSG and TEOS layers may be plasma etched under the following conditions:

| | | |
|----------------------|------------------|--------|
| Pressure: | 30 mT | |
| RF Power: | 500 W | |
| Magnetic Field: | 40 Gauss | |
| Cathode Temperature: | 20 Celsius | |
| Gas Flows: | CF ₄ | 20sccm |
| | CHF ₃ | 25sccm |

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| | |
|--------------------------------|---------|
| CH ₂ F ₂ | 20sccm |
| Ar | 160sccm |

5 The etching of the BPSG and TEOS layers can be also achieved by a wet etch first, followed by a dry etch. As such, removal of the BPSG layer leaving the TEOS layer is accomplished by using a wet etch, for example a 30:1 acetic acid/hydrofluoric acid solution that will etch first the BPSG selective to the nitride caps and the TEOS oxide. Subsequent to the wet etch, a typical dry etch is applied. The dry etch then etches the TEOS oxide layer selective to the nitride cap.

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15 At this point, a normal silicide gate stack structure, such as structure 62 of Figures 12 and 13, having a nitride cap 60 is left. The silicide gate stack structure 62 may now be used in a conventional implant process where the gate structure is needed to mask the dopant implantation of the source/drain regions of the adjacent transistors defined by the gate stacks. Next, the gate stacks are prepared to undergo a standard SAC etch.

20 Referring now to Figure 14, the next step in the flow process is the nitride spacer deposition. The nitride regions 32 of Figures 2 and 3 correspond to nitride spacers 64 of Figure 14. The silicide gate stack structures 62, protected by nitride spacers 64, are further subjected to a spacer etch to remove silicon nitride from the surface of substrate 12, leaving spacers 64a and 64b as shown in Figure 15.

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 Referring to Figure 16, an oxide layer 24, for example BPSG or the like, is now deposited over the substrate 12 and the silicide gate stack structures 62, which are protected by nitride caps 64a and 64b. To create a contact

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opening 70 into semiconductor substrate 12 through oxide layer 24, a photoresist material 26 is deposited and patterned using conventional photolithography steps. As illustrated in Figure 17, after patterning and subsequent oxide etching, the self-aligned contact hole 70 is created.

5 Conventional processing steps can now be carried out to form a conductor in contact hole 70 and other structures necessary to produce a semiconductor device, for example, a memory device.

The above description illustrates preferred embodiments which achieve the features and advantages of the present invention. It is not intended that the present invention be limited to the illustrated embodiments. Modifications and substitutions to specific process conditions and structures can be made without departing from the spirit and scope of the present invention. Accordingly, the invention is not to be considered as being limited by the foregoing description and drawings, but is only limited by the scope of the 15 appended claims.

What is claimed is:

1. A gate structure for a semiconductor device, comprising:

a gate oxide formed on a semiconductor substrate;

5 a conductive gate formed on said gate oxide;

a silicide layer formed on said conductive gate; and

10 an etch protecting cap formed over a top surface of said silicide gate, said cap being sufficient to protect said conductive gate and silicide layer from being etched during a self-aligned contact etching process, employing said gate structure.

2. The gate structure of claim 1, wherein said silicide layer is

formed by a salicide process.

15 3. The gate structure of claim 2, wherein said cap is formed of

silicon-based insulator.

4. The gate structure of claim 3, wherein said insulator is

selected from the group consisting of silicon nitride and silicon oxide.

20 5. The gate structure of claim 3, wherein said cap has a

thickness within the range of approximately 1000 to 2000 Angstroms.

6. The gate structure of claim 2, wherein said conductive gate

25 is formed of polysilicon.

7. The gate structure of claim 6, wherein said polysilicon gate

has a thickness within the range of approximately 500 to 1500 Angstroms.

8. The gate structure of claim 2, wherein said silicide layer is formed from a metal selected from the group consisting of cobalt, titanium, tungsten, tantalum, molybdenum, and platinum.

5 9. The gate structure of claim 2, wherein said silicide layer has a thickness within the range of approximately 200 to 500 Angstroms.

10 10. The gate structure of claim 2 further comprising an insulating spacer on side walls of said gate structure.

11. The gate structure of claim 10, wherein said insulating spacer is formed of silicon nitride.

12. A method for forming a gate structure for a semiconductor device, comprising:

forming a gate oxide on a semiconductor substrate;
forming a conductive gate on said gate oxide;
forming a silicide layer on said conductive gate by a salicide method;
and

20 forming an etch protective cap over a top surface of said silicide gate, said cap being sufficient to protect said conductive gate and silicide layer from being etched during a self-aligned contact etching process, employing said gate structure.

25 13. The method of claim 12, wherein said cap is formed of silicon-based insulator.

14. The method of claim 13, wherein said insulator is selected from the group consisting of silicon nitride and silicon oxide.

15. The method of claim 13, wherein said cap has a thickness within the range of approximately 1000 to 2000 Angstroms.

5 16. The method of claim 12, wherein said conductive gate is formed of polysilicon.

17. The method of claim 16, wherein said polysilicon gate has a thickness within the range of approximately 500 to 1500 Angstroms.

10 18. The method of claim 12, wherein said silicide layer is formed from a metal selected from the group consisting of cobalt, titanium, tungsten, tantalum, molybdenum, and platinum.

15 19. The method of claim 12, wherein said silicide layer has a thickness within the range of approximately 200 to 500 Angstroms.

20 20. The method of claim 12 further comprising an insulating spacer on side walls of said gate structure.

21. The method of claim 20, wherein said insulating spacer is formed of silicon nitride.

25 22. The method of claim 12, wherein said self-aligned contact etching process comprises etching an insulating layer in said semiconductor substrate with an etchant selected from the group consisting of C₂F₆, CH₄, C₃F₈, C₄H₁₀, C₂F₈, CH₂F₂, CHF₃, C₂HF₅, and CH₃F.

23. The method of claim 22, wherein said etching of said insulating layer is a reactive ion etch (RIE) employing a composition comprising a CF₄/ CHF₃/ CH₂F₂/ Ar gas mixture at volume ratio 1:1:1:8.

5 24. A method for forming features of a semiconductor device, comprising:

forming a gate stack on a semiconductor substrate, said gate stack including an oxide layer provided on said substrate, a conductive layer over said oxide layer, a silicide layer over said conductive layer formed by a salicide process and a cap layer over said silicide layer; and

10 providing an insulating layer over said substrate and said gate stack; and

performing a self-aligned contact etch of said insulating layer using said gate stack to align said etch.

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25. The method of claim 24, wherein said step of performing a self-aligned contact etch comprises etching said insulating layer with an etchant selected from the group consisting of C₂F₆, CH₄, C₃F₈, C₄H₁₀, C₂F₈, CH₂F₂, CHF₃, C₂HF₅, and CH₃F.

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26. The method of claim 25, wherein said etching of said insulating layer is a reactive ion etch (RIE) employing a composition comprising a CF₄/ CHF₃/ CH₂F₂/ Ar gas mixture at volume ratio 1:1:1:8.

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27. The method of claim 24, wherein said cap layer of said gate stack is formed of silicon-based insulator.

28. The method of claim 27, wherein said insulator is selected from the group consisting of silicon nitride and silicon oxide.

29. The method of claim 24, wherein said cap layer of said gate stack has a thickness within the range of approximately 1000 to 2000 Angstroms.

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30. The method of claim 24, wherein said conductive layer of said gate stack is formed of polysilicon.

10 31. The method of claim 30, wherein said polysilicon layer has a thickness within the range of approximately 500 to 1500 Angstroms.

32. The method of claim 24, wherein said silicide layer is formed from a metal selected from the group consisting of cobalt, titanium, tungsten, tantalum, molybdenum, and platinum.

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33. The method of claim 24, wherein said silicide layer has a thickness within the range of approximately 200 to 500 Angstroms.

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34. A method for forming a gate structure for a semiconductor device, comprising:

forming an insulating layer over a substrate;

masking said insulating layer to define an etching area on top of said insulating layer;

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etching said insulating layer at said etching area down to a top surface of said substrate to form an opening into said insulating layer;

forming a gate oxide layer on said substrate at the bottom of said opening;

depositing a polysilicon layer over said gate oxide layer;

etching said polysilicon layer to form a polysilicon gate over said gate oxide layer;

depositing a refractory metal over said polysilicon gate;

converting said refractory metal to a silicide layer over said polysilicon gate;

5 forming an etch protective cap over a top surface of said silicide layer; and

etching away said insulating layer to leave a gate stack comprising said oxide layer, said polysilicon gate, said silicide layer, and said protective cap.

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35. The method of claim 34, wherein said cap is sufficient to protect said conductive gate and silicide layer from being etched during a self-aligned contact etching process, employing said gate structure.

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36. The method of claim 34 further comprising forming a barrier layer over said substrate prior to the formation of said insulating layer over said substrate.

20

37. The method of claim 36 further comprising etching away of said barrier layer.

38. The method of claim 34, wherein said insulating layer is selected from the group consisting of BPSG, BSG, and PSG.

25

39. The method of claim 34, wherein said barrier layer is TEOS.

40. The method of claim 34, wherein etching of said insulating layer to form said opening employs a reactive ion etch (RIE).

hydride ion"); (b) hydrogen atom ("ordinary hydrogen atom"), 13.6 eV; (c) diatomic hydrogen molecule, 15.46 eV ("ordinary hydrogen molecule"); (d) hydrogen molecular ion, 16.4 eV ("ordinary hydrogen molecular ion"); and (e) H_3^+ , 22.6 eV ("ordinary trihydrogen molecular ion"). Herein, with reference to forms of hydrogen, "normal" and "ordinary" are synonymous.

According to a further preferred embodiment of the invention, a compound is provided comprising at least one increased binding energy hydrogen species such as (a) a hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$, preferably within $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (b) a hydride ion (H^-) having a binding energy of about

$$\frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1+\sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi\mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1+\sqrt{s(s+1)}}{p} \right]^3} \right), \text{ preferably within } \pm 10\%, \text{ more preferably } \pm 5\%, \text{ where } p \text{ is an integer, preferably an integer from 2 to 200, } s = 1/2, \pi \text{ is pi, } \hbar \text{ is Planck's constant bar, } \mu_0 \text{ is the permeability of vacuum, } m_e \text{ is the mass of the electron, } \mu_e \text{ is the reduced electron mass, } a_0 \text{ is the Bohr radius, and } e \text{ is the elementary charge; (c) } H_4^+(1/p); \text{ (d) a trihydrino molecular ion, } H_3^+(1/p), \text{ having a binding energy of about } \frac{22.6}{\left(\frac{1}{p}\right)^2} \text{ eV}$$

preferably within $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (e) a dihydrino having a binding energy of about $\frac{15.5}{\left(\frac{1}{p}\right)^2} \text{ eV}$ preferably within $\left(\frac{1}{p}\right)$

$\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (f) a dihydrino molecular ion with a binding energy of about $\frac{16.4}{\left(\frac{1}{p}\right)^2} \text{ eV}$ preferably within $\pm 10\%$, more

preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200.

According to one embodiment of the invention wherein the compound comprises a negatively charged increased binding energy hydrogen species, the compound further comprises one or more cations, such as a proton, ordinary H_2^+ , or ordinary H_3^+ .

A method is provided for preparing compounds comprising at least one increased binding energy hydride ion. Such compounds are hereinafter referred to as "hydrino hydride compounds". The method comprises reacting atomic hydrogen with a catalyst having a net enthalpy of reaction of about $\frac{m}{2} \cdot 27 \text{ eV}$, where m is an integer greater than 1, preferably an integer less than 400, to produce an increased binding energy hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where

p is an integer, preferably an integer from 2 to 200. A further product of the catalysis is energy. The increased binding energy hydrogen atom can be reacted with an electron source, to produce an increased binding energy hydride ion. The increased binding energy hydride ion can be reacted with one or more cations to produce a compound comprising at least one increased binding energy hydride ion.

4. Hydride Reactor

The invention is also directed to a reactor for producing increased binding energy hydrogen compounds of the invention, such as hydrino hydride compounds. A further product of the catalysis is energy. Such a reactor is hereinafter referred to as a "hydrino hydride reactor". The hydrino hydride reactor comprises a cell for making hydrinos and an electron source. The reactor produces hydride ions having the binding energy of Eq. (36). The cell for making hydrinos may take the form of a gas cell, a gas discharge cell, or a plasma torch cell, for example. Each of these cells comprises: a source of atomic hydrogen; at least one of a solid, molten, liquid, or gaseous catalyst for

making hydrinos; and a vessel for reacting hydrogen and the catalyst for making hydrinos. As used herein and as contemplated by the subject invention, the term "hydrogen", unless specified otherwise, includes not only protium (1H), but 5 also deuterium (2H) and tritium (3H). Electrons from the electron source contact the hydrinos and react to form hydrino hydride ions.

The reactors described herein as "hydrino hydride reactors" are capable of producing not only hydrino hydride ions 10 and compounds, but also the other increased binding energy hydrogen compounds of the present invention. Hence, the designation "hydrino hydride reactors" should not be understood as being limiting with respect to the nature of the increased binding energy hydrogen compound produced.

According to one aspect of the present invention, novel 15 compounds are formed from hydrino hydride ions and cations. In the gas cell, the cation can be an oxidized species of the material of the cell, a cation comprising the molecular hydrogen dissociation material which produces atomic hydrogen, a cation 20 comprising an added reductant, or a cation present in the cell (such as a cation comprising the catalyst). In the discharge cell, the cation can be an oxidized species of the material of the cathode or anode, a cation of an added reductant, or a cation 25 present in the cell (such as a cation comprising the catalyst). In the plasma torch cell, the cation can be either an oxidized species of the material of the cell, a cation of an added reductant, or a cation present in the cell (such as a cation comprising the catalyst).

30 **5. DATA**

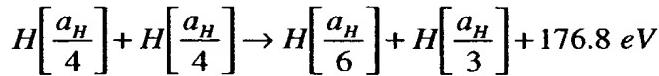
A high voltage discharge of hydrogen with and without the presence of a source of potassium, potassium iodide, in the discharge was performed with a hollow cathode at the Institut Fur Niedertemperatur-Plasmaphysik e.V. [R. Mills, "Observation 35 of Extreme Ultraviolet Emission from Hydrogen-KI Plasmas Produced by a Hollow Cathode Discharge", Int. J. Hydrogen Energy, in press, "Mills-INP"] which is herein incorporated by

reference. It has been reported that intense extreme ultraviolet (EUV) emission was observed from atomic hydrogen and certain elements or certain ions which ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV [R. Mills, J. Dong, Y. 5 Lu, "Observation of Extreme Ultraviolet Hydrogen Emission from Incandescently Heated Hydrogen Gas with Certain Catalysts", Int. J. Hydrogen Energy, Vol. 25, (2000), pp. 919-943 which is incorporated herein by reference]. Two potassium ions or a potassium atom may each provide an electron ionization or 10 transfer reaction that has a net enthalpy equal to an integer multiple of 27.2 eV. In the Mills-INP study, the spectral lines of atomic hydrogen were intense enough to be recorded on photographic films only when KI was present. EUV lines not assignable to potassium, iodine, or hydrogen shown in TABLE 3 15 were observed at 73.0, 132.6, 513.6, 677.8, 885.9, and 1032.9 Å. The lines could be assigned to transitions of atomic hydrogen to lower energy levels corresponding to lower energy hydrogen atoms called hydrino atoms and the emission from the excitation of the corresponding hydride ions formed from the hydrino 20 atoms.

TABLE 3. Observed emission data from hydrogen-KI plasmas produced by a hollow cathode discharge that can not be assigned to atomic or molecular hydrogen.

| Peak | INP Peak # | Observed Wave-length (Å) | Observed Energy (eV) | Peak Assignment | Predicted Energy (eV) | Predicted Wave-length (Å) |
|---------------|---------------|--------------------------|----------------------|---|-----------------------|---------------------------|
| 1 (inside) | # 24, # 30 | 73.0 | 169.9 | 1/4 → 1/6 H transition ^a | 176.8 | 70.2 |
| 3 | # 30 | 1032.9 | 12.0 | H ⁻ (1/4) ^{b,c} | 11.23 | 1104 |
| 19 | # 28 | 132.6 | 93.5 | 1/4 → 1/5 H transition ^d | 95.2 | 130.3 |
| 20 | # 28 | 885.9 | 14.0 | Inelastic H scattering of H * $\left[\frac{a_H}{4} \right]$ ^e | 13.98 | 887.2 |
| 21 | # 30 | 513.6 | 25.15 | H ⁻ (1/6) ^c | 22.8 | 543 |
| 22 | # 30 | 677.8 | 18.30 | H ⁻ (1/5) ^c | 16.7 | 742 |

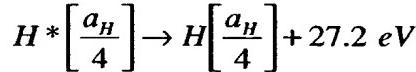
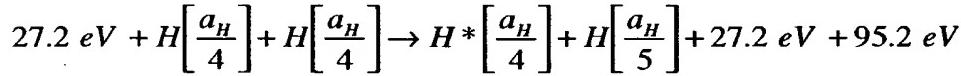
^a Transition induced by a resonance state excited in $H\left[\frac{a_H}{4}\right]$



^b I⁺ has a peak at 1034.66 Å, [31] but none of the other iodine lines were detected including much stronger lines.

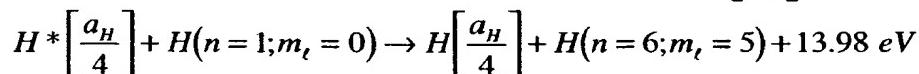
^c The hydride ion emission is anticipated to be shift to shorter wavelengths due to its presence in a chemical compound.

^d Transition induced by a metastable state excited in $H\left[\frac{a_H}{4}\right]$



¹⁰ $H\left[\frac{a_H}{4}\right] \rightarrow H\left[\frac{a_H}{5}\right] + 95.2 \text{ eV} + 27.2 \text{ eV}$

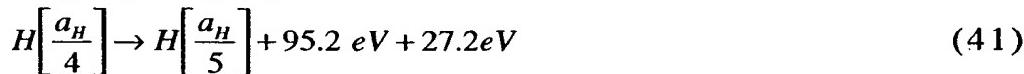
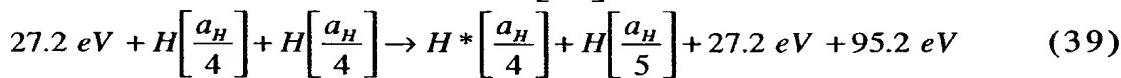
^e Hydrogen inelastic scattered peak of $H^*\left[\frac{a_H}{4}\right]$ deexcitation



¹⁵ The results support that potassium atoms reacted with atomic hydrogen to form novel hydrogen energy states.

Potassium iodide present in the discharge of hydrogen served as a source of potassium metal which was observed to collect on the walls of the cell during operation. According to Eqs. (3-5), potassium metal reacts with atomic hydrogen present in the
 5 discharge and forms the hydrino atom $H\left[\frac{a_H}{4}\right]$. The energy released was expected to undergo *internal conversion* to increase the brightness of the plasma discharge since this is the common mechanism of relaxation. This is consistent with observation.

10 The product, $H\left[\frac{a_H}{4}\right]$ may serve as a reactant to form $H\left[\frac{a_H}{5}\right]$ according to Eqs. (29-31). The transition of $H\left[\frac{a_H}{4}\right]$ to $H\left[\frac{a_H}{5}\right]$ induced by a resonance transfer of 27.21 eV, $m=1$ in Eq. (2) with a metastable state excited in $H\left[\frac{a_H}{4}\right]$ is represented by

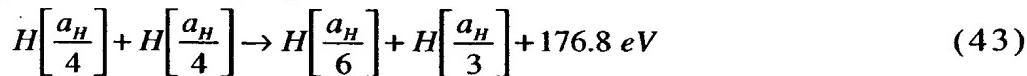


The energy emitted by a hydrino which has nonradiatively transferred $m \times 27.2 \text{ eV}$ of energy to a second hydrino may be emitted as a spectral line. Hydrinos may accept energy by a
 20 nonradiative mechanism [Mills GUT]; thus, rather than suppressing the emission through internal conversion they do not interact with the emitted radiation. The predicted 95.2 eV (130.3 Å) photon (peak # 19) shown in FIGURE 29 of Mills-INP is a close match with the observed 132.6 Å line. In FIGURE 29 of Mills-INP, an additional peak (peak #20) was observed at 885.9 Å. It is proposed that peak #20 of Mills-INP arises from inelastic hydrogen scattering of the metastable state $H^*\left[\frac{a_H}{4}\right]$
 25 formed by the resonant nonradiative energy transfer of 27.2 eV from a first $H\left[\frac{a_H}{4}\right]$ atom to a second as shown in Eq. (39). The
 30 metastable state then nonradiatively transfers part of the

27.2 eV excitation energy to excite atomic hydrogen initially in the state $1s^2S_{1/2}$ to the state $6h^2H_{11/2}$. This leaves a 13.98 eV (887.2 Å) photon, peak 20. The initial and final states for all hydrogen species and emitted photons are determined by the selection rule for conservation of angular momentum where the 13.98 eV photon corresponds to $m_t = 0$ and the initial and final states for the hydrino atom reactants correspond to $m_t = 3$ and $m_t = -2$, respectively. In the case that the 95.2 eV (130.3 Å) photon (peak # 19) corresponds to $m_t = 0$ or ± 1 , then angular momentum is conserved. The excited state hydrogen may then emit hydrogen lines that are observed in FIGURE 29 of Mills-INP. Thus, the inelastic hydrogen scattering of the deexcitation of $H^*\left[\frac{a_H}{4}\right]$ may be represented by

$$H^*\left[\frac{a_H}{4}\right](m_t = 3) + H(n = 1; m_t = 0) \rightarrow H\left[\frac{a_H}{4}\right](m_t = -2) + H(n = 6; m_t = 5) + 13.98 \text{ eV}(m_t = 0) \quad (42)$$

The product of the catalysis of atomic hydrogen with potassium metal, $H\left[\frac{a_H}{4}\right]$, may serve as reactants to form $H\left[\frac{a_H}{3}\right]$ and $H\left[\frac{a_H}{6}\right]$ according to Eq. (32). The transition of $H\left[\frac{a_H}{4}\right]$ to $H\left[\frac{a_H}{6}\right]$ induced by a multipole resonance transfer of 54.4 eV, $m = 2$ in Eq. (2) and a transfer of 40.8 eV with a resonance state of $H\left[\frac{a_H}{3}\right]$ excited in $H\left[\frac{a_H}{4}\right]$ is represented by



The predicted 176.8 eV (70.2 Å) photon is a close match with the observed 73.0 Å line of Mills-INP.

The hydrinos are predicted to form hydrino hydride ions. A novel inorganic hydride compound *KHI* which comprises high binding energy hydride ions was synthesized by reaction of atomic hydrogen with potassium metal and potassium iodide [R. Mills, B. Dhandapani, N. Greenig, J. He, "Synthesis and Characterization of Potassium Iodo Hydride", Int. J. of Hydrogen Energy, Vol. 25, Issue 12, December, (2000), pp. 1185-1203].

The X-ray photoelectron spectroscopy (XPS) spectrum of *KHI* differed from that of *KI* by having additional features at 9.1 eV and 11.1 eV. The XPS peaks centered at 9.0 eV and 11.1 eV that do not correspond to any other primary element peaks may 5 correspond to the $H^-(n=1/4)$ $E_b = 11.2$ eV hydride ion predicted by Mills [Mills GUT] (Eq. (36)) in two different chemical environments where E_b is the predicted vacuum binding energy. In this case, the reaction to form $H^-(n=1/4)$ is given by Eqs. (3- 10 5) and Eq. (38). Hydrino hydride ions $H^-(n=1/4)$, $H^-(n=1/5)$, and $H^-(n=1/6)$ corresponding to the corresponding hydrino atoms were anticipated. The predicted energy of emission due to these ions in the plasma discharge was anticipated to be higher than that given in TABLE 2 due to the formation of stable compounds such as *KHI* comprising these ions. Emission peaks 15 which could not be assigned to hydrogen, potassium, or iodine were observed at 1032.9 Å (12.0 eV), 677.8 Å (18.3 eV), and 513.6 Å (24.1 eV) [Mills-INP]. The binding energies of hydrino hydride ions $H^-(n=1/4)$, $H^-(n=1/5)$, and $H^-(n=1/6)$ corresponding to the corresponding hydrino atoms are 11.23 eV, 20 16.7 eV, and 22.81 eV. The emissions were 1 to 2 eV higher than predicted which may be due to the presence of these ions in compounds with chemical environments different from that of vacuum. The excitation was due to the plasma electron bombardment.

CLAIMS

1. A method of producing light, plasma, power, or compounds containing lower energy hydrogen comprising a reaction of lower energy atomic hydrogen whereby a catalyzed lower energy hydrogen atom serves as a reactant of a disproportionation reaction whereby it which accepts energy from an second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes a nonradiative electronic transition to a higher nonionized energy level while the second undergoes a transition to a lower energy level.
2. The method of claim 1 whereby lower-energy hydrogen atoms are generated by the catalysis of atomic hydrogen.
3. The method of claim 2 whereby the catalysis of atomic hydrogen comprises the reaction of atomic hydrogen with a catalyst that provides a net enthalpy of reaction of an integer multiple of 27.2 eV to form a hydrogen atom having a binding energy of $\text{Binding Energy} = \frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where p is an integer greater than 1, preferably from 2 to 200.
4. The method of claim 3 wherein the catalyst is selected from the group of Li, Be, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Kr, Rb, Sr, Nb, Mo, Pd, Sn, Te, Cs, Ce, Pr, Sm, Gd, Dy, Pb, Pt, He^+ , Na^+ , Rb^+ , Fe^{3+} , Mo^{2+} , Mo^{4+} , In^{3+} , He^+ , Ar^+ , Xe^+ , Ar^{2+} and H^+ , and Ne^+ and H^+ and K^+ and K^+ .
5. The method of claim 1 further comprising a metastable excitation, resonance excitation, or ionization of a hydrino atom involving a nonradiative energy transfer between lower energy atoms of hydrogen of $m \times 27.2 \text{ eV}$ where m is an integer.
6. The method of claim 5 whereby the resonant transfer

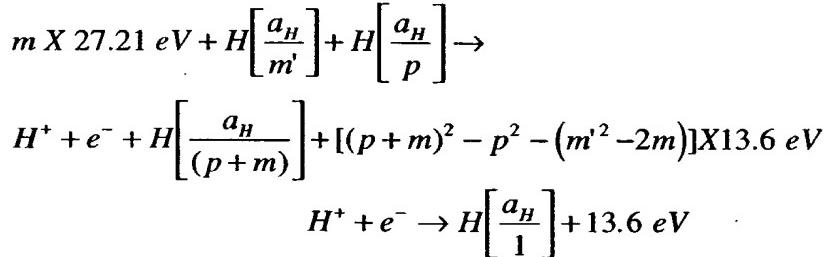
occurs in multiple stages.

7. The method of claim 1 comprising the transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced by a resonance transfer of $m \cdot 27.21 \text{ eV}$ with a metastable state excited in $H\left[\frac{a_H}{p'}\right]$ which is represented by
- $$m \cdot 27.2 \text{ eV} + H\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p}\right] \rightarrow H^*\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p+m}\right] + [(p+m)^2 - p^2] X 13.6 \text{ eV}$$
- $$H^*\left[\frac{a_H}{p'}\right] \rightarrow H\left[\frac{a_H}{p'}\right] + m \cdot 27.2 \text{ eV}$$
- And, the overall reaction is
- $$H\left[\frac{a_H}{p}\right] \rightarrow H\left[\frac{a_H}{p+m}\right] + [(p+m)^2 - p^2] X 13.6 \text{ eV}$$
- where p , p' , and m are integers and the asterisk represents an excited metastable state.

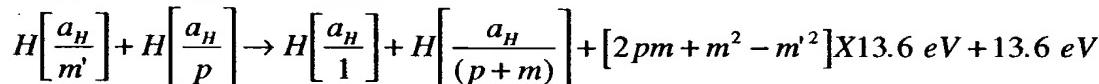
8. The method of claim 1 comprising the transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced by a multipole resonance transfer of $m \cdot 27.21 \text{ eV}$ and a transfer of $[(p')^2 - (p'-m')^2] X 13.6 \text{ eV} - m \cdot 27.2 \text{ eV}$ with a resonance state of $H\left[\frac{a_H}{p'-m'}\right]$ excited in $H\left[\frac{a_H}{p'}\right]$ which is represented by
- $$H\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p}\right] \rightarrow$$
- $$H\left[\frac{a_H}{p'-m'}\right] + H\left[\frac{a_H}{p+m}\right] + [((p+m)^2 - p^2) - (p'^2 - (p'-m')^2)] X 13.6 \text{ eV}$$
- where p , p' , m , and m' are integers.

- 20 9. The method of claim 5 comprising a disproportionation reaction whereby the transition cascade for the p th cycle of the hydrogen-type atom, $H\left[\frac{a_H}{p}\right]$, with the hydrogen-type atom,

$H\left[\frac{a_H}{m'}\right]$, that is ionized as the source of a net enthalpy of reaction of $mX 27.2 \text{ eV}$ where m is an integer that causes the transition is represented by



And, the overall reaction is



10 10. The method of claim 1 wherein a lower energy hydrogen compound is produced comprising

(a) at least one neutral, positive, or negative increased binding energy hydrogen species having a binding energy

(i) greater than the binding energy of the corresponding ordinary hydrogen species, or

15 (ii) greater than the binding energy of any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' binding energy is less than thermal energies at ambient conditions, or is negative; and

20 (b) at least one other element.

11. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the group consisting of H_n , H_n^- , and H_n^+ where n is a positive integer, with the proviso that n is greater than 1 when H has a positive charge.

25 12. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the

group consisting of (a) hydride ion having a binding energy that is greater than the binding of ordinary hydride ion (about 0.8 eV) for $p=2$ up to 23 in which the binding energy is represented

$$\text{by Binding Energy} = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right)$$

- 5 where p is an integer greater than one, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge; (b) hydrogen atom having a binding energy greater than about 13.6 eV; (c)
10 hydrogen molecule having a first binding energy greater than about 15.5 eV; and (d) molecular hydrogen ion having a binding energy greater than about 16.4 eV.

13. A method of claim 12 wherein the lower energy hydrogen
15 compound is produced which is characterized in that the increased binding energy hydrogen species is a hydride ion having a binding energy of about 3.0, 6.6, 11.2, 16.7, 22.8, 29.3, 36.1, 42.8, 49.4, 55.5, 61.0, 65.6, 69.2, 71.5, 72.4, 71.5, 68.8, 64.0, 56.8, 47.1, 34.6, 19.2, or 0.65 eV.

- 20 14. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is a hydride ion having the binding energy:

$$25 \quad \text{Binding Energy} = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right)$$

- where p is an integer greater than one, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge.

15. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the group consisting of

- 5 (a) a hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where p is an integer,
- (b) an increased binding energy hydride ion (H^-) having a binding energy of about

10
$$\frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right)$$
 where $s = 1/2$, π is

pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge;

- 15 (c) an increased binding energy hydrogen species $H_4^+(1/p)$;
- (d) an increased binding energy hydrogen species trihydrino molecular ion, $H_3^+(1/p)$, having a binding energy of about $\frac{22.6}{\left(\frac{1}{p}\right)^2} \text{ eV}$ where p is an integer,
- (e) an increased binding energy hydrogen molecule having a binding energy of about $\frac{15.5}{\left(\frac{1}{p}\right)^2} \text{ eV}$; and
- 20 (f) an increased binding energy hydrogen molecular ion with a binding energy of about $\frac{16.4}{\left(\frac{1}{p}\right)^2} \text{ eV}$.

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A3

(54) Title: HYDROGEN CATALYSIS

WO 01/70627

(57) Abstract: A catalytic reaction of atomic hydrogen is provided which produces a more stable or lower energy atomic hydrogen atom than uncatalyzed atomic hydrogen. The catalyzed lower energy hydrogen atom may serve as a reactant of a disproportionation reaction whereby it which accepts energy from a second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes a nonradiative electronic transition to a higher energy level while the second undergoes a transition to a lower energy level. The catalytic reaction and disproportionation reaction of lower energy atomic hydrogen may produce light, plasma, power, and novel hydrogen compounds. The light, plasma, power and compound source comprises a cell for the catalysis of atomic hydrogen and disproportionation reactions of lower energy atomic hydrogen to form novel hydrogen species and compositions of matter comprising hydrogen that is more stable or lower energy than uncatalyzed hydrogen. The compounds comprise at least one neutral, positive, or negative hydrogen species having a binding energy greater than its corresponding ordinary hydrogen species, or greater than any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/JS 01/09055

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G21K1/00 H05G2/00

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B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| P, X | MILLS R L: "The hydrogen atom revisited" INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, ELSEVIER SCIENCE PUBLISHERS B.V., BARKING, GB, vol. 25, no. 12, December 2000 (2000-12), pages 1171-1183, XP004221042 ISSN: 0360-3199 cited in the application page 1178, paragraph 6 --- | 1-5 |
| Y | WO 00 07932 A (MILLS RANDELL L) 17 February 2000 (2000-02-17) cited in the application page 2, line 11 -page 5, line 6 claims 1-6 --- | 7-15 |
| Y | WO 00 07932 A (MILLS RANDELL L) 17 February 2000 (2000-02-17) cited in the application page 2, line 11 -page 5, line 6 claims 1-6 --- | 7-15 |
| A | --- | 1-5 |
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

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|---|--|
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 22 October 2001 | 30/10/2001 |
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| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016 | Capostagno, E |

INTERNATIONAL SEARCH REPORT

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|------------------------------|
| International Application No |
| PCT/US 01/09055 |

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | MILLS R L: "NOVEL HYDROGEN COMPOUNDS FROM A POTASSIUM CARBONATE ELECTROLYTIC CELL" FUSION TECHNOLOGY, AMERICAN NUCLEAR SOCIETY, LAGRANGE PARK, ILLINOIS, US, vol. 37, no. 2, March 2000 (2000-03), pages 157-181, XP000920328 ISSN: 0748-1896 cited in the application page 157, left-hand column, paragraph 1 -page 159, left-hand column, paragraph 1 ----- | 1-4 |
| A | MILLS R L ET AL: "Fractional quantum energy levels of hydrogen" FUSION TECHNOLOGY, NOV. 1995, USA, vol. 28, no. 4, pages 1697-1719, XP001016098 ISSN: 0748-1896 cited in the application page 1702, left-hand column, paragraph 1 -right-hand column, last paragraph page 1713, right-hand column, last paragraph ----- | 1-4 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/09055

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|-------------------------|------------|------------------|
| WO 0007932 | A 17-02-2000 | AU | 1308100 A | 28-02-2000 |
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| | | EP | 1100746 A2 | 23-05-2001 |
| | | WO | 0007931 A2 | 17-02-2000 |
| | | WO | 0007932 A2 | 17-02-2000 |

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(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,



A2

(54) Title: HYDROGEN CATALYSIS

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HYDROGEN CATALYSIS

I. INTRODUCTION

5 1. Field of the Invention:

This invention is hydrogen reactions which may produce light, plasma, power, and novel hydrogen compounds. The light, plasma, power, and compound source comprises a cell for the catalysis of atomic hydrogen to form novel hydrogen species and compositions of matter comprising more stable hydrogen than uncatalyzed hydrogen. The catalyzed atomic hydrogen may react to cause electronic transitions involving a nonradiative energy transfer mechanism with a net release of energy and the formation of hydrogen containing compositions of matter of further increased stability.

2. Background of the Invention

2.1 Hydrogen Plasma

A historical motivation to cause EUV emission from a hydrogen gas was that the spectrum of hydrogen was first recorded from the only known source, the Sun. Developed sources that provide a suitable intensity are high voltage discharge, synchrotron, and inductively coupled plasma generators. An important variant of the later type of source is a tokomak that operates at temperatures in the tens of millions of degrees.

2.2 Hydride Ions

A hydride ion comprises two indistinguishable electrons bound to a proton. Alkali and alkaline earth hydrides react violently with water to release hydrogen gas which burns in air ignited by the heat of the reaction with water. Typically metal hydrides decompose upon heating at a temperature well below the melting point of the parent metal.

II. SUMMARY OF THE INVENTION

An objective of the present invention is to generate a plasma and a source light such as visible and high energy light such as extreme ultraviolet light via the catalysis of atomic
5 hydrogen.

Another objective is to react hydrogen with a catalyst to form more stable hydrogen than uncatalyzed hydrogen. The more stable lower energy hydrogen may serve as reactants to form lower energy hydrogen of further stability.
10

Another objective is to form novel hydride compounds comprising more stable hydrogen than uncatalyzed hydrogen.

1 Hydrinos

A hydrogen atom having a binding energy given by
15

$$\text{Binding Energy} = \frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2} \quad (1)$$

where p is an integer greater than 1, preferably from 2 to 200, is disclosed in R. Mills, *The Grand Unified Theory of Classical Quantum Mechanics*, January 2000 Edition, BlackLight Power, Inc., Cranbury, New Jersey, Distributed by Amazon.com (" '00
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35 Dr. Behram N. Kursunoglu, Chairman, December 14-17, 2000,

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pp. 669-683; R. Mills, B. Dhandapani, M. Nansteel, J. He, T. Shannon, A. Echezuria, "Synthesis and Characterization of Novel Hydride Compounds", Int. J. of Hydrogen Energy, in press; R. Mills, "Highly Stable Novel Inorganic Hydrides", Journal of Materials Research, submitted; R. Mills, "Novel Hydrogen Compounds from a Potassium Carbonate Electrolytic Cell", Fusion Technology, Vol. 37, No. 2, March, (2000), pp. 157-182; R. Mills, "The Hydrogen Atom Revisited", Int. J. of Hydrogen Energy, Vol. 25, Issue 12, December, (2000), pp. 1171-1183; Mills, R., Good, W., "Fractional Quantum Energy Levels of Hydrogen", Fusion Technology, Vol. 28, No. 4, November, (1995), pp. 1697-1719; Mills, R., Good, W., Shaubach, R., "Dihydrino Molecule Identification", Fusion Technology, Vol. 25, 103 (1994); R. Mills and S. Kneizys, Fusion Technol. Vol. 20, 65 (1991); and in prior PCT applications PCT/US00/20820; PCT/US00/20819; PCT/US99/17171; PCT/US99/17129; PCT/US 98/22822; PCT/US98/14029; PCT/US96/07949; PCT/US94/02219; PCT/US91/8496; PCT/US90/1998; and prior US Patent Applications Ser. No. 09/225,687, filed on January 6, 1999; Ser. No. 60/095,149, filed August 3, 1998; Ser. No. 60/101,651, filed September 24, 1998; Ser. No. 60/105,752, filed October 26, 1998; Ser. No. 60/113,713, filed December 24, 1998; Ser. No. 60/123,835, filed March 11, 1999; Ser. No. 60/130,491, filed April 22, 1999; Ser. No. 60/141,036, filed June 29, 1999; Serial No. 09/009,294 filed January 20, 1998; Serial No. 09/111,160 filed July 7, 1998; Serial No. 09/111,170 filed July 7, 1998; Serial No. 09/111,016 filed July 7, 1998; Serial No. 09/111,003 filed July 7, 1998; Serial No. 09/110,694 filed July 7, 1998; Serial No. 09/110,717 filed July 7, 1998; Serial No. 60/053378 filed July 22, 1997; Serial No. 60/068913 filed December 29, 1997; Serial No. 60/090239 filed June 22, 1998; Serial No. 09/009455 filed January 20, 1998; Serial No. 09/110,678 filed July 7, 1998; Serial No. 60/053,307 filed July 22, 1997; Serial No. 60/068918 filed December 29, 1997; Serial No. 60/080,725 filed April 3, 1998; Serial No. 09/181,180 filed October 28, 1998; Serial No. 60/063,451 filed October 29, 1997; Serial No. 09/008,947 filed January 20, 1998; Serial No. 60/074,006 filed

February 9, 1998; Serial No. 60/080,647 filed April 3, 1998; Serial No. 09/009,837 filed January 20, 1998; Serial No. 08/822,170 filed March 27, 1997; Serial No. 08/592,712 filed January 26, 1996; Serial No. 08/467,051 filed on June 6, 1995; 5 Serial No. 08/416,040 filed on April 3, 1995; Serial No. 08/467,911 filed on June 6, 1995; Serial No. 08/107,357 filed on August 16, 1993; Serial No. 08/075,102 filed on June 11, 1993; Serial No. 07/626,496 filed on December 12, 1990; Serial No. 07/345,628 filed April 28, 1989; Serial No. 07/341,733 filed 10 April 21, 1989 the entire disclosures of which are all incorporated herein by reference (hereinafter "Mills Prior Publications"). The binding energy, of an atom, ion or molecule, also known as the ionization energy, is the energy required to remove one electron from the atom, ion or molecule.

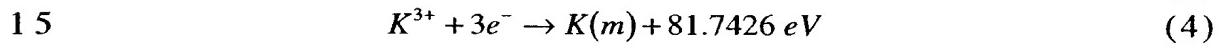
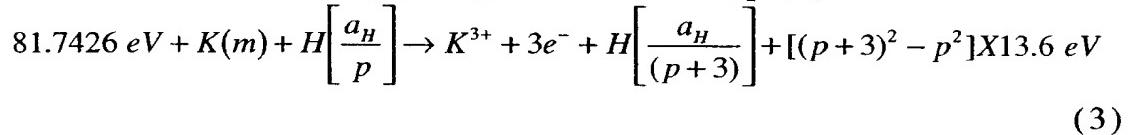
15 A hydrogen atom having the binding energy given in Eq. (1) is hereafter referred to as a hydrino atom or hydrino. The designation for a hydrino of radius $\frac{a_H}{p}$, where a_H is the radius of an ordinary hydrogen atom and p is an integer, is $H\left[\frac{a_H}{p}\right]$. A hydrogen atom with a radius a_H is hereinafter referred to as 20 "ordinary hydrogen atom" or "normal hydrogen atom." Ordinary atomic hydrogen is characterized by its binding energy of 13.6 eV.

Hydrinos are formed by reacting an ordinary hydrogen atom with a catalyst having a net enthalpy of reaction of about 25 $m \cdot 27.2 \text{ eV}$ (2)

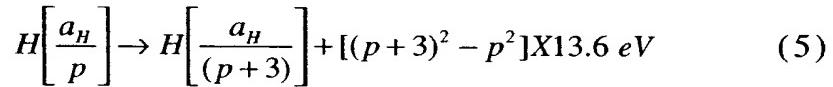
where m is an integer. This catalyst has also been referred to as an energy hole or source of energy hole in Mills earlier filed Patent Applications. It is believed that the rate of catalysis is increased as the net enthalpy of reaction is more closely 30 matched to $m \cdot 27.2 \text{ eV}$. It has been found that catalysts having a net enthalpy of reaction within $\pm 10\%$, preferably $\pm 5\%$, of $m \cdot 27.2 \text{ eV}$ are suitable for most applications.

This catalysis releases energy from the hydrogen atom with a commensurate decrease in size of the hydrogen atom, 35 $r_n = n a_H$. For example, the catalysis of $H(n=1)$ to $H(n=1/2)$

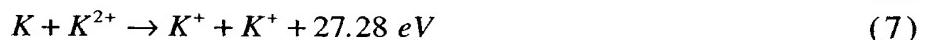
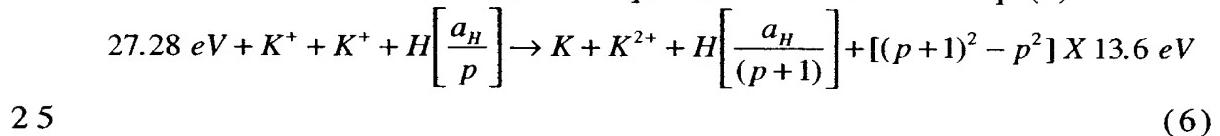
releases 40.8 eV , and the hydrogen radius decreases from a_H to $\frac{1}{2}a_H$. A catalytic system is provided by the ionization of t electrons from an atom each to a continuum energy level such that the sum of the ionization energies of the t electrons is 5 approximately $m \times 27.2 \text{ eV}$ where m is an integer. One such catalytic system involves potassium metal. The first, second, and third ionization energies of potassium are 4.34066 eV , 31.63 eV , 45.806 eV , respectively [D. R. Linde, CRC Handbook of Chemistry and Physics, 78 th Edition, CRC Press, Boca Raton, 10 Florida, (1997), p. 10-214 to 10-216]. The triple ionization ($t=3$) reaction of K to K^{3+} , then, has a net enthalpy of reaction of 81.7426 eV , which is equivalent to $m=3$ in Eq. (2).



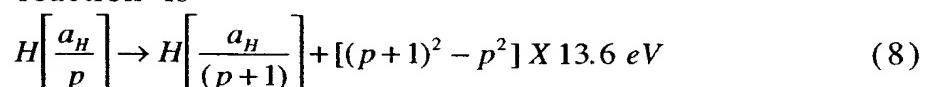
And, the overall reaction is



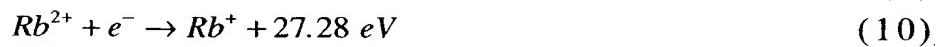
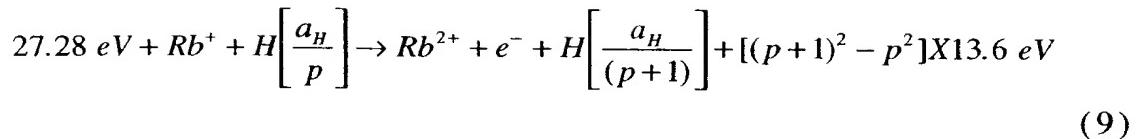
Potassium ions can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. 20 The second ionization energy of potassium is 31.63 eV ; and K^+ releases 4.34 eV when it is reduced to K . The combination of reactions K^+ to K^{2+} and K^+ to K , then, has a net enthalpy of reaction of 27.28 eV , which is equivalent to $m=1$ in Eq. (2).



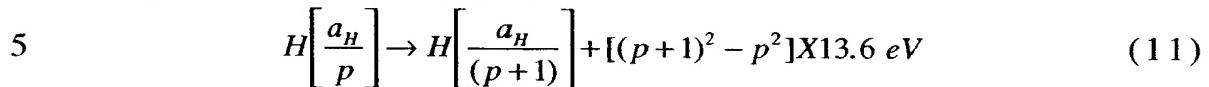
The overall reaction is



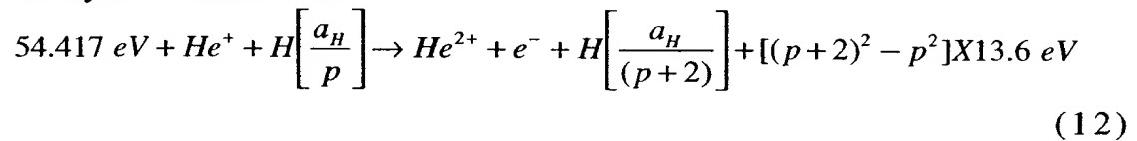
Rubidium ion (Rb^+) is also a catalyst because the second 30 ionization energy of rubidium is 27.28 eV . In this case, the catalysis reaction is



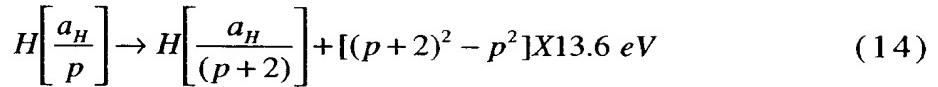
And, the overall reaction is



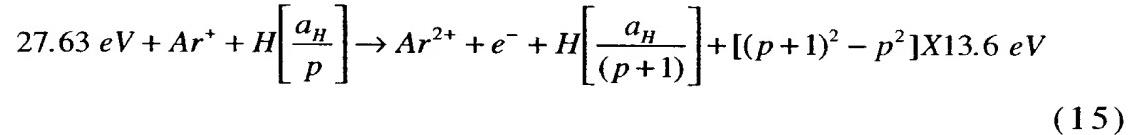
Helium ion (He^+) is also a catalyst because the second ionization energy of helium is 54.417 eV. In this case, the catalysis reaction is



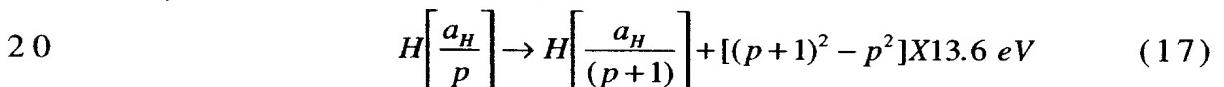
And, the overall reaction is



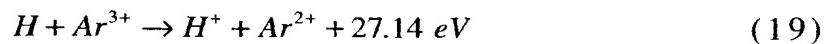
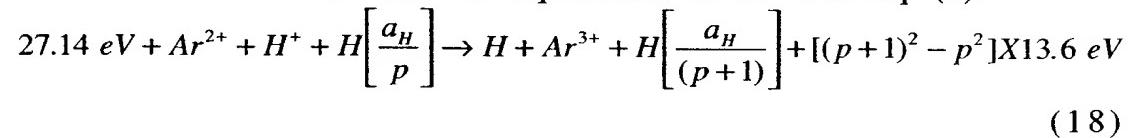
Argon ion is a catalyst. The second ionization energy is
15 27.63 eV.



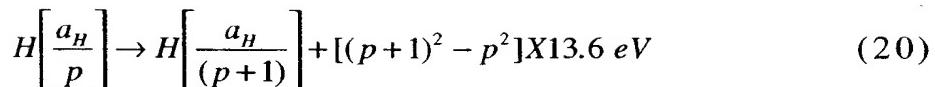
And, the overall reaction is



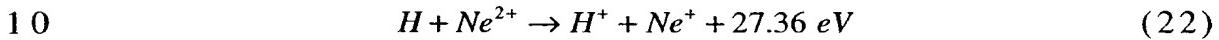
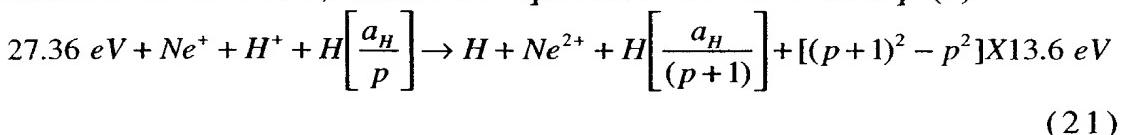
An argon ion and a proton can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The third ionization energy of argon is 40.74 eV, and H^+ releases 13.6 eV when it is reduced to H . The combination of reactions of Ar^{2+} to Ar^{3+} and H^+ to H , then, has a net enthalpy of reaction of 27.14 eV, which is equivalent to $m=1$ in Eq. (2).



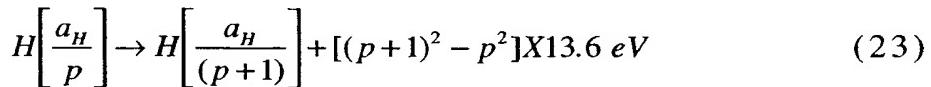
30 And, the overall reaction is



An neon ion and a proton can also provide a net enthalpy of a multiple of that of the potential energy of the hydrogen atom. The second ionization energy of neon is 40.96 eV, and H^+ releases 13.6 eV when it is reduced to H . The combination of reactions of Ne^+ to Ne^{2+} and H^+ to H , then, has a net enthalpy of reaction of 27.36 eV, which is equivalent to $m=1$ in Eq. (2).



And, the overall reaction is



The energy given off during catalysis is much greater than the energy lost to the catalyst. The energy released is large as compared to conventional chemical reactions. For example, when hydrogen and oxygen gases undergo combustion to form water



the known enthalpy of formation of water is $\Delta H_f = -286 \text{ kJ/mole}$ or 1.48 eV per hydrogen atom. By contrast, each ($n=1$) ordinary hydrogen atom undergoing catalysis releases a net of 40.8 eV.

Moreover, further catalytic transitions may occur:

$n = \frac{1}{2} \rightarrow \frac{1}{3}, \frac{1}{3} \rightarrow \frac{1}{4}, \frac{1}{4} \rightarrow \frac{1}{5}$, and so on. Once catalysis begins,

hydrinos autocatalyze further in a process called disproportionation. This mechanism is similar to that of an inorganic ion catalysis. But, hydrino catalysis should have a higher reaction rate than that of the inorganic ion catalyst due to the better match of the enthalpy to $m \cdot 27.2 \text{ eV}$.

2. Disproportionation

Lower-energy hydrogen atoms, "hydrinos", may be generated by the catalysis of atomic hydrogen by a catalyst such as at least one of the catalysts given in Eqs. (3-23). The

catalyzed lower energy hydrogen atom may serve as a reactant of a disproportionation reaction whereby it which accepts energy from an second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes 5 a nonradiative electronic transition to a higher energy level while the second undergoes a transition to a lower energy level.

3. Novel Hydrogen Compounds

Lower energy atomic hydrogen may react to form a compound 10 comprising

- (a) at least one neutral, positive, or negative increased binding energy hydrogen species having a binding energy
 - (i) greater than the binding energy of the corresponding ordinary hydrogen species, or
 - (ii) greater than the binding energy of any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' binding energy is less than thermal energies at ambient conditions, or is negative; and
- 20 (b) at least one other element.

IV. DETAILED DESCRIPTION OF THE INVENTION

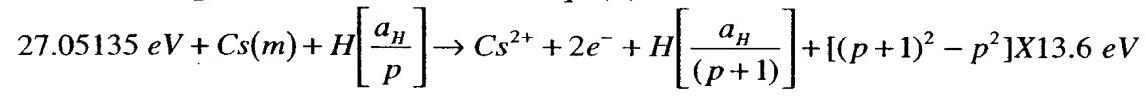
1. Catalysts

25 The above objectives and other objectives are achieved by the present invention of a catalytic reaction of hydrogen to form more stable atomic hydrogen than uncatalyzed hydrogen which may serve as reactants to form lower energy hydrogen of further stability to provide a light, plasma, power, and novel 30 hydrogen compound source. The light, plasma, power, and novel hydrogen compound source comprises a cell for the catalysis of atomic hydrogen to form novel hydrogen species and compositions of matter comprising new forms of hydrogen.

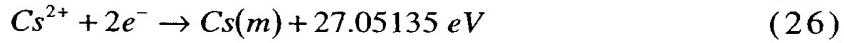
In an embodiment, a catalytic system is provided by the 35 ionization of t electrons from a participating species such as an atom, an ion, a molecule, and an ionic or molecular compound to a continuum energy level such that the sum of the ionization

energies of the t electrons is approximately $m \times 27.2 \text{ eV}$ where m is an integer. One such catalytic system involves cesium. The first and second ionization energies of cesium are 3.89390 eV and 23.15745 eV , respectively [David R. Linde, CRC Handbook of

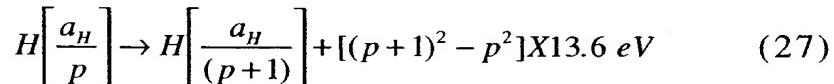
5 Chemistry and Physics, 74 th Edition, CRC Press, Boca Raton, Florida, (1993), p. 10-207]. The double ionization ($t=2$) reaction of Cs to Cs^{2+} , then, has a net enthalpy of reaction of 27.05135 eV , which is equivalent to $m=1$ in Eq. (2).



10 (25)



And, the overall reaction is



Thermal energies may broaden the enthalpy of reaction. The
15 relationship between kinetic energy and temperature is given by

$$E_{kinetic} = \frac{3}{2}kT \quad (28)$$

For a temperature of 1200 K, the thermal energy is 0.16 eV, and the net enthalpy of reaction provided by cesium metal
20 is 27.21 eV which is an exact match to the desired energy.

Hydrogen catalysts capable of providing a net enthalpy of reaction of approximately $m \times 27.2 \text{ eV}$ where m is an integer to produce hydrino whereby t electrons are ionized from an atom or ion are given *infra*. A further product of the catalysis is
25 energy. The atoms or ions given in the first column are ionized to provide the net enthalpy of reaction of $m \times 27.2 \text{ eV}$ given in the tenth column where m is given in the eleventh column. The electrons which are ionized are given with the ionization potential (also called ionization energy or binding energy). The
30 ionization potential of the n th electron of the atom or ion is designated by IP_n and is given by David R. Linde, CRC Handbook of Chemistry and Physics, 78 th Edition, CRC Press, Boca Raton, Florida, (1997), p. 10-214 to 10-216 which is herein incorporated by reference. That is for example,

$Cs + 3.89390 \text{ eV} \rightarrow Cs^+ + e^-$ and $Cs^+ + 23.15745 \text{ eV} \rightarrow Cs^{2+} + e^-$. The first ionization potential, $IP_1 = 3.89390 \text{ eV}$, and the second ionization potential, $IP_2 = 23.15745 \text{ eV}$, are given in the second and third columns, respectively. The net enthalpy of reaction for the double ionization of Cs is 27.05135 eV as given in the tenth column, and $m=1$ in Eq. (2) as given in the eleventh column.

TABLE 1. Hydrogen Catalysts

| Catalyst | IP1 | IP2 | IP3 | IP4 | IP5 | IP6 | IP7 | IP8 | Enthalpy | m |
|----------|--------|---------|--------|--------|--------|--------|-------|-----|----------|----|
| Li | 5.3917 | 5.6402 | | | | | | | 81.032 | 3 |
| Be | 9.3226 | 8.2112 | | | | | | | 27.534 | 1 |
| K | 4.3406 | 1.63 | 45.806 | | | | | | 81.777 | 3 |
| Ca | 6.1131 | 1.871 | 0.913 | 67.27 | | | | | 136.17 | 5 |
| Ti | 6.8282 | 13.575 | 27.491 | 43.267 | 99.3 | | | | 190.46 | 7 |
| V | 6.7463 | 14.66 | 29.311 | 46.709 | 65.281 | | | | 162.71 | 6 |
| | | | | | | 7 | | | | |
| Cr | 6.7666 | 46.485 | 30.96 | | | | | | 54.212 | 2 |
| Mn | 7.4340 | 25.64 | 33.668 | 51.2 | | | | | 107.94 | 4 |
| Fe | 7.9024 | 16.187 | 30.652 | | | | | | 54.742 | 2 |
| Fe | 7.9024 | 16.187 | 30.652 | 54.8 | | | | | 109.54 | 4 |
| Co | 7.881 | 17.083 | 33.5 | 51.3 | | | | | 109.76 | 4 |
| Co | 7.881 | 17.083 | 33.5 | 51.3 | 79.5 | | | | 189.26 | 7 |
| Ni | 7.6398 | 18.168 | 35.19 | 54.9 | 76.06 | | | | 191.96 | 7 |
| Ni | 7.6398 | 18.168 | 35.19 | 54.9 | 76.06 | 108 | | | 299.96 | 11 |
| Cu | 7.7263 | 20.2924 | | | | | | | 28.019 | 1 |
| Zn | 9.3940 | 57.9644 | | | | | | | 27.358 | 1 |
| Zn | 9.3940 | 57.964 | 49.723 | 59.4 | 82.6 | 108 | 134 | 174 | 625.08 | 23 |
| As | 9.8152 | 18.633 | 28.351 | 50.13 | 62.63 | 127.6 | | | 297.16 | 11 |
| Se | 9.7523 | 21.19 | 30.820 | 42.945 | 68.3 | 81.7 | 155.4 | | 410.11 | 15 |
| Kr | 13.999 | 24.359 | 36.95 | 52.5 | 64.7 | 78.5 | | | 271.01 | 10 |
| Kr | 13.999 | 24.359 | 36.95 | 52.5 | 64.7 | 78.5 | 111 | | 382.01 | 14 |
| Rb | 4.1771 | 27.285 | 40 | 52.6 | 71 | 84.4 | 99.2 | | 378.66 | 14 |
| Rb | 4.1771 | 27.285 | 40 | 52.6 | 71 | 84.4 | 99.2 | 136 | 514.66 | 19 |
| Sr | 5.6948 | 41.030 | 42.89 | 57 | 71.6 | | | | 188.21 | 7 |
| Nb | 6.7588 | 54.32 | 25.04 | 38.3 | 50.55 | | | | 134.97 | 5 |
| Mo | 7.0924 | 36.16 | 27.13 | 46.4 | 54.49 | 68.827 | | | 151.27 | 8 |

| | | | | | | | | | | |
|------|---------|---------|----------|--------|-------|--------|--------|-----------|--------|----|
| Mo | 7.09243 | 6.16 | 27.13 | 46.4 | 54.49 | 68.827 | 125.66 | 143.6 | 489.36 | 18 |
| | | | | | | 6 | 4 | | | |
| Pd | 8.3369 | 19.43 | | | | | | 27.767 | 1 | |
| Sn | 7.3438 | 11.4632 | 30.5020 | 40.735 | 72.28 | | | 165.49 | 6 | |
| Te | 9.0096 | 18.6 | | | | | | 27.61 | 1 | |
| Te | 9.0096 | 18.6 | 27.96 | | | | | 55.57 | 2 | |
| Cs | 3.8939 | 23.1575 | | | | | | 27.051 | 1 | |
| Ce | 5.5387 | 10.85 | 20.198 | 36.758 | 65.55 | | | 138.89 | 5 | |
| Ce | 5.5387 | 10.85 | 20.198 | 36.758 | 65.55 | 77.6 | | 216.49 | 8 | |
| Pr | 5.464 | 10.55 | 21.624 | 38.98 | 57.53 | | | 134.15 | 5 | |
| Sm | 5.6437 | 11.07 | 23.4 | 41.4 | | | | 81.514 | 3 | |
| Gd | 6.15 | 12.09 | 20.63 | 44 | | | | 82.87 | 3 | |
| Dy | 5.9389 | 11.67 | 22.8 | 41.47 | | | | 81.879 | 3 | |
| Pb | 7.4166 | 615.032 | 31.9373 | | | | | 54.386 | 2 | |
| Pt | 8.9587 | 18.563 | | | | | | 27.522 | 1 | |
| He+ | | 54.4178 | | | | | | 54.418 | 2 | |
| Na+ | | 47.2864 | 71.620 | 88.91 | | | | 217.816 | 8 | |
| Rb+ | | 27.285 | | | | | | 27.285 | 1 | |
| Fe3+ | | | 54.8 | | | | | 54.8 | 2 | |
| Mo2+ | | 27.13 | | | | | | 27.13 | 1 | |
| Mo4+ | | | | 54.49 | | | | 54.49 | 2 | |
| In3+ | | | 54 | | | | | 54 | 2 | |
| Xe+ | | 21.209 | 732.1230 | | | | | 53.332792 | | |

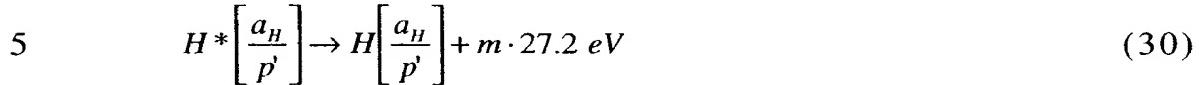
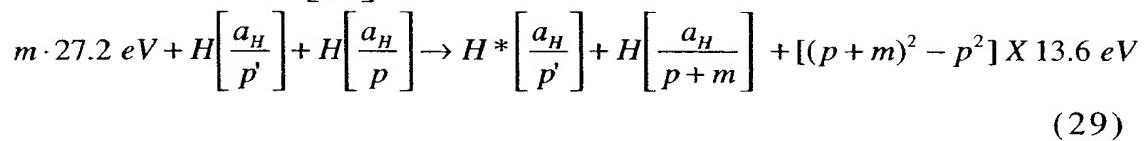
2. Disproportionation

Lower-energy hydrogen atoms, "hydrinos", may be generated by the catalysis of atomic hydrogen by a catalyst such as at least one of the catalysts given in Table 1. The catalyzed lower energy hydrogen atom may serve as a reactant of a disproportionation reaction whereby it which accepts energy from an second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes a nonradiative electronic transition to a higher energy level while the second undergoes a transition to a lower energy level. Lower-energy hydrogen atoms, "hydrinos", can act as reactants to cause electronic transitions of atomic hydrogen with a further

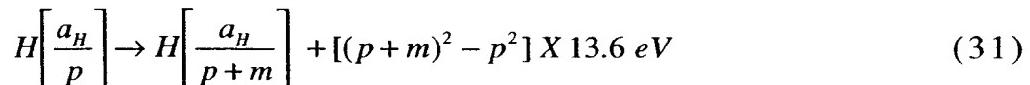
release of energy because each of the metastable excitation, resonance excitation, and ionization energy of a hydrino atom is $m \times 27.2 \text{ eV}$ (Eq. (2)). The transition reaction mechanism of a first hydrino atom affected by a second hydrino atom involves the resonant coupling between the atoms of m degenerate multipoles each having 27.21 eV of potential energy [Mills GUT]. The energy transfer of $m \times 27.2 \text{ eV}$ from the first hydrino atom to the second hydrino atom causes the central field of the first atom to increase by m and its electron to drop m levels lower from a radius of $\frac{a_H}{p}$ to a radius of $\frac{a_H}{p+m}$. The second interacting lower-energy hydrogen is either excited to a metastable state, excited to a resonance state, or ionized by the resonant energy transfer. The resonant transfer may occur in multiple stages. For example, a nonradiative transfer by multipole coupling may occur wherein the central field of the first increases by m , then the electron of the first drops m levels lower from a radius of $\frac{a_H}{p}$ to a radius of $\frac{a_H}{p+m}$ with further resonant energy transfer. The energy transferred by multipole coupling may occur by a mechanism that is analogous to photon absorption involving an excitation to a virtual level. Or, the energy transferred by multipole coupling and during the electron transition of the first hydrino atom may occur by a mechanism that is analogous to two photon absorption involving a first excitation to a virtual level and a second excitation to a resonant or continuum level [Thompson, B. J., Handbook of Nonlinear Optics, Marcel Dekker, Inc., New York, (1996), pp. 497-548; Shen, Y. R., The Principles of Nonlinear Optics, John Wiley & Sons, New York, (1984), pp. 203-210; B. de Beauvoir, F. Nez, L. Julien, B. Cagnac, F. Biraben, D. Touahri, L. Hilico, O. Acef, A. Clairon, and J. J. Zondy, Physical Review Letters, Vol. 78, No. 3, (1997), pp. 440-443]. The transition energy greater than the energy transferred to the second hydrino atom may appear as a photon in a vacuum medium.

For example, the transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced

by a resonance transfer of $m \cdot 27.21 \text{ eV}$ (Eq. (2)) with a metastable state excited in $H\left[\frac{a_H}{p'}\right]$ is represented by

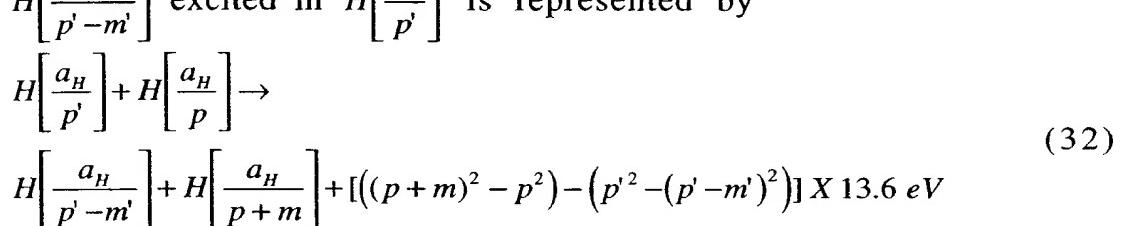


And, the overall reaction is



where p , p' , and m are integers and the asterisk represents an excited metastable state.

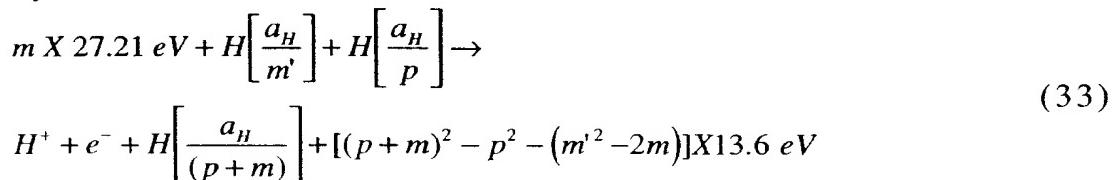
10 The transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced by a multipole resonance transfer of $m \cdot 27.21 \text{ eV}$ (Eq. (2)) and a transfer of $[(p')^2 - (p'-m')^2] \times 13.6 \text{ eV} - m \cdot 27.2 \text{ eV}$ with a resonance state of $H\left[\frac{a_H}{p'-m'}\right]$ excited in $H\left[\frac{a_H}{p'}\right]$ is represented by



where p , p' , m , and m' are integers.

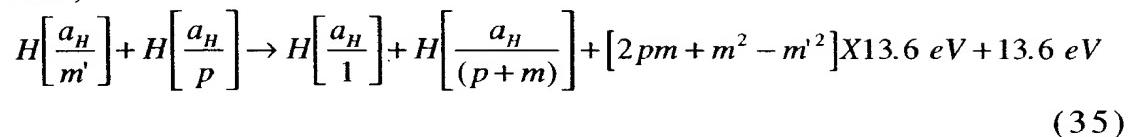
The second lower-energy hydrogen may be ionized by the resonant nonradiative energy transfer of an integer multiple of 27.21 eV . The transition cascade for the p th cycle of the hydrogen-type atom, $H\left[\frac{a_H}{p}\right]$, with the hydrogen-type atom,

20 $H\left[\frac{a_H}{m'}\right]$, that is ionized as the source of a net enthalpy of reaction of $m \times 27.2 \text{ eV}$ (Eq. (2)) that causes the transition is represented by





And, the overall reaction is



5

3. Catalysis of Hydrogen to Form Novel Hydrogen Species and Compositions of Matter Comprising New Forms of Hydrogen

The catalytic reaction of hydrogen forms novel hydrogen species and compositions of matter comprising new forms of

10 hydrogen. The novel hydrogen compositions of matter comprise:

(a) at least one neutral, positive, or negative hydrogen species (hereinafter "increased binding energy hydrogen species") having a binding energy

15 (i) greater than the binding energy of the corresponding ordinary hydrogen species, or

(ii) greater than the binding energy of any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' binding energy is less than thermal energies at ambient 20 conditions (standard temperature and pressure, STP), or is negative; and

(b) at least one other element. The compounds of the invention are hereinafter referred to as "increased binding energy hydrogen compounds".

25 By "other element" in this context is meant an element other than an increased binding energy hydrogen species. Thus, the other element can be an ordinary hydrogen species, or any element other than hydrogen. In one group of compounds, the other element and the increased binding energy hydrogen

30 species are neutral. In another group of compounds, the other element and increased binding energy hydrogen species are charged such that the other element provides the balancing charge to form a neutral compound. The former group of compounds is characterized by molecular and coordinate bonding;

35 the latter group is characterized by ionic bonding.

Also provided are novel compounds and molecular ions comprising

- (a) at least one neutral, positive, or negative hydrogen species (hereinafter "increased binding energy hydrogen species") having a total energy
- 5 (i) greater than the total energy of the corresponding ordinary hydrogen species, or
 - (ii) greater than the total energy of any hydrogen species for which the corresponding ordinary hydrogen species
- 10 is unstable or is not observed because the ordinary hydrogen species' total energy is less than thermal energies at ambient conditions, or is negative; and
- (b) at least one other element.

The total energy of the hydrogen species is the sum of the energies to remove all of the electrons from the hydrogen species. The hydrogen species according to the present invention has a total energy greater than the total energy of the corresponding ordinary hydrogen species. The hydrogen species having an increased total energy according to the present invention is also referred to as an "increased binding energy hydrogen species" even though some embodiments of the hydrogen species having an increased total energy may have a first electron binding energy less than the first electron binding energy of the corresponding ordinary hydrogen species. For example, the hydride ion of Eq. (36) for $p=24$ has a first binding energy that is less than the first binding energy of ordinary hydride ion, while the total energy of the hydride ion of Eq. (36) for $p=24$ is much greater than the total energy of the corresponding ordinary hydride ion.

30 Also provided are novel compounds and molecular ions comprising

- (a) a plurality of neutral, positive, or negative hydrogen species (hereinafter "increased binding energy hydrogen species") having a binding energy
- 35 (i) greater than the binding energy of the corresponding ordinary hydrogen species, or
- (ii) greater than the binding energy of any hydrogen

species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' binding energy is less than thermal energies at ambient conditions or is negative; and

- 5 (b) optionally one other element. The compounds of the invention are hereinafter referred to as "increased binding energy hydrogen compounds".

The increased binding energy hydrogen species can be formed by reacting one or more hydrino atoms with one or more 10 of an electron, hydrino atom, a compound containing at least one of said increased binding energy hydrogen species, and at least one other atom, molecule, or ion other than an increased binding energy hydrogen species.

Also provided are novel compounds and molecular ions 15 comprising

(a) a plurality of neutral, positive, or negative hydrogen species (hereinafter "increased binding energy hydrogen species") having a total energy

20 (i) greater than the total energy of ordinary molecular hydrogen, or

(ii) greater than the total energy of any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' total energy is less than thermal energies at ambient 25 conditions or is negative; and

(b) optionally one other element. The compounds of the invention are hereinafter referred to as "increased binding energy hydrogen compounds".

The total energy of the increased total energy hydrogen species 30 is the sum of the energies to remove all of the electrons from the increased total energy hydrogen species. The total energy of the ordinary hydrogen species is the sum of the energies to remove all of the electrons from the ordinary hydrogen species. The increased total energy hydrogen species is referred to as an 35 increased binding energy hydrogen species, even though some of the increased binding energy hydrogen species may have a first electron binding energy less than the first electron binding

energy of ordinary molecular hydrogen. However, the total energy of the increased binding energy hydrogen species is much greater than the total energy of ordinary molecular hydrogen.

5 In one embodiment of the invention, the increased binding energy hydrogen species can be H_n , and H_n^- where n is a positive integer, or H_n^+ where n is a positive integer greater than one. Preferably, the increased binding energy hydrogen species is H_n and H_n^- where n is an integer from one to about 1×10^6 , more
10 preferably one to about 1×10^4 , even more preferably one to about 1×10^2 , and most preferably one to about 10, and H_n^+ where n is an integer from two to about 1×10^6 , more preferably two to about 1×10^4 , even more preferably two to about 1×10^2 , and most preferably two to about 10. A specific example of H_n^-
15 is H_{16}^- .

In an embodiment of the invention, the increased binding energy hydrogen species can be H_n^{m-} where n and m are positive integers and H_n^{m+} where n and m are positive integers with $m < n$. Preferably, the increased binding energy hydrogen species is
20 H_n^{m-} where n is an integer from one to about 1×10^6 , more preferably one to about 1×10^4 , even more preferably one to about 1×10^2 , and most preferably one to about 10 and m is an integer from one to 100, one to ten, and H_n^{m+} where n is an integer from two to about 1×10^6 , more preferably two to about
25 1×10^4 , even more preferably two to about 1×10^2 , and most preferably two to about 10 and m is one to about 100, preferably one to ten.

According to a preferred embodiment of the invention, a compound is provided, comprising at least one increased binding
30 energy hydrogen species selected from the group consisting of (a) hydride ion having a binding energy according to Eq. (36) that is greater than the binding of ordinary hydride ion (about 0.8 eV) for $p=2$ up to 23, and less for $p=24$ ("increased binding energy hydride ion" or "hydrino hydride ion"); (b) hydrogen atom having a binding energy greater than the binding energy of ordinary hydrogen atom (about 13.6 eV) ("increased binding energy hydrogen atom" or "hydrino"); (c) hydrogen molecule

having a first binding energy greater than about 15.5 eV ("increased binding energy hydrogen molecule" or "dihydrino"); and (d) molecular hydrogen ion having a binding energy greater than about 16.4 eV ("increased binding energy molecular hydrogen ion" or "dihydrino molecular ion").

The compounds of the present invention are capable of exhibiting one or more unique properties which distinguishes them from the corresponding compound comprising ordinary hydrogen, if such ordinary hydrogen compound exists. The unique properties include, for example, (a) a unique stoichiometry; (b) unique chemical structure; (c) one or more extraordinary chemical properties such as conductivity, melting point, boiling point, density, and refractive index; (d) unique reactivity to other elements and compounds; (e) enhanced stability at room temperature and above; and/or (f) enhanced stability in air and/or water. Methods for distinguishing the increased binding energy hydrogen-containing compounds from compounds of ordinary hydrogen include: 1.) elemental analysis, 2.) solubility, 3.) reactivity, 4.) melting point, 5.) boiling point, 6.) vapor pressure as a function of temperature, 7.) refractive index, 8.) X-ray photoelectron spectroscopy (XPS), 9.) gas chromatography, 10.) X-ray diffraction (XRD), 11.) calorimetry, 12.) infrared spectroscopy (IR), 13.) Raman spectroscopy, 14.) Mossbauer spectroscopy, 15.) extreme ultraviolet (EUV) emission and absorption spectroscopy, 16.) ultraviolet (UV) emission and absorption spectroscopy, 17.) visible emission and absorption spectroscopy, 18.) nuclear magnetic resonance spectroscopy, 19.) gas phase mass spectroscopy of a heated sample (solids probe and direct exposure probe quadrupole and magnetic sector mass spectroscopy), 20.) time-of-flight-secondary-ion-mass-spectroscopy (TOFSIMS), 21.) electrospray-ionization-time-of-flight-mass-spectroscopy (ESITOFMS), 22.) thermogravimetric analysis (TGA), 23.) differential thermal analysis (DTA), 24.) differential scanning calorimetry (DSC), 25.) liquid chromatography/mass spectroscopy (LCMS), 26.) neutron diffraction, and/or 27.) gas chromatography/mass spectroscopy (GCMS).

According to the present invention, a hydrino hydride ion (H^-) having a binding energy according to Eq. (36) that is greater than the binding of ordinary hydride ion (about 0.8 eV) for $p=2$ up to 23, and less for $p=24$ (H^-) is provided. For $p=2$ to $p=24$ of 5 Eq. (36), the hydride ion binding energies are respectively 3, 6.6, 11.2, 16.7, 22.8, 29.3, 36.1, 42.8, 49.4, 55.5, 61.0, 65.6, 69.2, 71.5, 72.4, 715, 68.8, 64.0, 56.8, 47.1, 34.6, 19.2, and 0.65 eV. Compositions comprising the novel hydride ion are also provided.

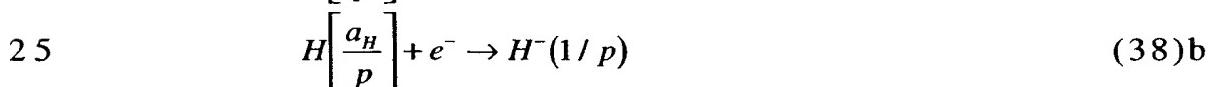
10 The binding energy of the novel hydrino hydride ion can be represented by the following formula:

$$\text{Binding Energy} = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right) \quad (36)$$

where p is an integer greater than one, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge. The radii are given by 15

$$r_2 = r_1 = a_0 \left(1 + \sqrt{s(s+1)} \right); s = \frac{1}{2} \quad (37)$$

The hydrino hydride ion of the present invention can be 20 formed by the reaction of an electron source with a hydrino, that is, a hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{n^2}$, where $n = \frac{1}{p}$ and p is an integer greater than 1. The hydrino hydride ion is represented by $H^-(n=1/p)$ or $H^-(1/p)$:



The hydrino hydride ion is distinguished from an ordinary hydride ion comprising an ordinary hydrogen nucleus and two electrons having a binding energy of about 0.8 eV. The latter is hereafter referred to as "ordinary hydride ion" or "normal 30 hydride ion". The hydrino hydride ion comprises a hydrogen

nucleus including protium, deuterium, or tritium, and two indistinguishable electrons at a binding energy according to Eq. (36).

The binding energies of the hydrino hydride ion,
5 $H^- (n=1/p)$ as a function of p , where p is an integer, are shown in TABLE 2.

TABLE 2. The representative binding energy of the hydrino hydride ion $H^-(n=1/p)$ as a function of p , Eq. (36).

| | Hydride Ion (a_o) ^a | r_1 Energy (eV) ^b | Binding (nm) | Wavelength |
|----|---------------------------------------|-----------------------------------|-----------------|------------|
| 5 | $H^-(n=1/2)$ | 0.9330 | 3.047 | 407 |
| | $H^-(n=1/3)$ | 0.6220 | 6.610 | 188 |
| | $H^-(n=1/4)$ | 0.4665 | 11.23 | 110 |
| | $H^-(n=1/5)$ | 0.3732 | 16.70 | 74.2 |
| | $H^-(n=1/6)$ | 0.3110 | 22.81 | 54.4 |
| | $H^-(n=1/7)$ | 0.2666 | 29.34 | 42.3 |
| | $H^-(n=1/8)$ | 0.2333 | 36.08 | 34.4 |
| | $H^-(n=1/9)$ | 0.2073 | 42.83 | 28.9 |
| | $H^-(n=1/10)$ | 0.1866 | 49.37 | 25.1 |
| 10 | $H^-(n=1/11)$ | 0.1696 | 55.49 | 22.3 |
| | $H^-(n=1/12)$ | 0.1555 | 60.97 | 20.3 |
| | $H^-(n=1/13)$ | 0.1435 | 65.62 | 18.9 |
| | $H^-(n=1/14)$ | 0.1333 | 69.21 | 17.9 |
| | $H^-(n=1/15)$ | 0.1244 | 71.53 | 17.3 |
| | $H^-(n=1/16)$ | 0.1166 | 72.38 | 17.1 |
| 15 | $H^-(n=1/17)$ | 0.1098 | 71.54 | 17.33 |
| | $H^-(n=1/18)$ | 0.1037 | 68.80 | 18.02 |
| | $H^-(n=1/19)$ | 0.0982 | 63.95 | 19.39 |
| | $H^-(n=1/20)$ | 0.0933 | 56.78 | 21.83 |
| | $H^-(n=1/21)$ | 0.0889 | 47.08 | 26.33 |
| 20 | $H^-(n=1/22)$ | 0.0848 | 34.63 | 35.80 |
| | $H^-(n=1/23)$ | 0.0811 | 19.22 | 64.49 |
| | $H^-(n=1/24)$ | 0.0778 | 0.6535 | 1897 |
| | ^a Equation (37) | | | |
| | ^b Equation (36) | | | |

Novel compounds are provided comprising one or more hydrino hydride ions and one or more other elements. Such a compound is referred to as a hydrino hydride compound.

Ordinary hydrogen species are characterized by the following binding energies (a) hydride ion, 0.754 eV ("ordinary

hydride ion"); (b) hydrogen atom ("ordinary hydrogen atom"), 13.6 eV; (c) diatomic hydrogen molecule, 15.46 eV ("ordinary hydrogen molecule"); (d) hydrogen molecular ion, 16.4 eV ("ordinary hydrogen molecular ion"); and (e) H_3^+ , 22.6 eV
5 ("ordinary trihydrogen molecular ion"). Herein, with reference to forms of hydrogen, "normal" and "ordinary" are synonymous.

According to a further preferred embodiment of the invention, a compound is provided comprising at least one increased binding energy hydrogen species such as (a) a
10 hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$,

preferably within $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (b) a hydride ion (H^-) having a binding energy of about

$$\frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1+\sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1+\sqrt{s(s+1)}}{p} \right]^3} \right), \text{ preferably within}$$

15 $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge; (c) $H_4^+(1/p)$; (d) a trihydrino molecular
20 ion, $H_3^+(1/p)$, having a binding energy of about $\frac{22.6}{\left(\frac{1}{p}\right)^2} \text{ eV}$

preferably within $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (e) a dihydrino having a binding energy of about $\frac{15.5}{\left(\frac{1}{p}\right)^2} \text{ eV}$ preferably within

25 $\pm 10\%$, more preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200; (f) a dihydrino molecular ion with a binding energy of about $\frac{16.4}{\left(\frac{1}{p}\right)^2} \text{ eV}$ preferably within $\pm 10\%$, more

preferably $\pm 5\%$, where p is an integer, preferably an integer from 2 to 200.

According to one embodiment of the invention wherein the compound comprises a negatively charged increased binding energy hydrogen species, the compound further comprises one or more cations, such as a proton, ordinary H_2^+ , or ordinary H_3^+ .

A method is provided for preparing compounds comprising at least one increased binding energy hydride ion. Such compounds are hereinafter referred to as "hydrino hydride compounds". The method comprises reacting atomic hydrogen with a catalyst having a net enthalpy of reaction of about $\frac{m}{2} \cdot 27 \text{ eV}$, where m is an integer greater than 1, preferably an integer less than 400, to produce an increased binding energy hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where p is an integer, preferably an integer from 2 to 200. A further product of the catalysis is energy. The increased binding energy hydrogen atom can be reacted with an electron source, to produce an increased binding energy hydride ion. The increased binding energy hydride ion can be reacted with one or more cations to produce a compound comprising at least one increased binding energy hydride ion.

4. Hydride Reactor

The invention is also directed to a reactor for producing increased binding energy hydrogen compounds of the invention, such as hydrino hydride compounds. A further product of the catalysis is energy. Such a reactor is hereinafter referred to as a "hydrino hydride reactor". The hydrino hydride reactor comprises a cell for making hydrinos and an electron source. The reactor produces hydride ions having the binding energy of Eq. (36). The cell for making hydrinos may take the form of a gas cell, a gas discharge cell, or a plasma torch cell, for example. Each of these cells comprises: a source of atomic hydrogen; at least one of a solid, molten, liquid, or gaseous catalyst for

making hydrinos; and a vessel for reacting hydrogen and the catalyst for making hydrinos. As used herein and as contemplated by the subject invention, the term "hydrogen", unless specified otherwise, includes not only protium (1H), but 5 also deuterium (2H) and tritium (3H). Electrons from the electron source contact the hydrinos and react to form hydrino hydride ions.

The reactors described herein as "hydrino hydride reactors" are capable of producing not only hydrino hydride ions 10 and compounds, but also the other increased binding energy hydrogen compounds of the present invention. Hence, the designation "hydrino hydride reactors" should not be understood as being limiting with respect to the nature of the increased binding energy hydrogen compound produced.

15 According to one aspect of the present invention, novel compounds are formed from hydrino hydride ions and cations. In the gas cell, the cation can be an oxidized species of the material of the cell, a cation comprising the molecular hydrogen dissociation material which produces atomic hydrogen, a cation 20 comprising an added reductant, or a cation present in the cell (such as a cation comprising the catalyst). In the discharge cell, the cation can be an oxidized species of the material of the cathode or anode, a cation of an added reductant, or a cation present in the cell (such as a cation comprising the catalyst). In 25 the plasma torch cell, the cation can be either an oxidized species of the material of the cell, a cation of an added reductant, or a cation present in the cell (such as a cation comprising the catalyst).

30 5. DATA

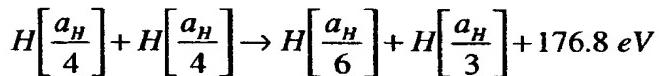
A high voltage discharge of hydrogen with and without the presence of a source of potassium, potassium iodide, in the discharge was performed with a hollow cathode at the Institut Fur Niedertemperatur-Plasmaphysik e.V. [R. Mills, "Observation 35 of Extreme Ultraviolet Emission from Hydrogen-KI Plasmas Produced by a Hollow Cathode Discharge", Int. J. Hydrogen Energy, in press, "Mills-INP"] which is herein incorporated by

reference. It has been reported that intense extreme ultraviolet (EUV) emission was observed from atomic hydrogen and certain elements or certain ions which ionize at integer multiples of the potential energy of atomic hydrogen, 27.2 eV [R. Mills, J. Dong, Y. 5 Lu, "Observation of Extreme Ultraviolet Hydrogen Emission from Incandescently Heated Hydrogen Gas with Certain Catalysts", Int. J. Hydrogen Energy, Vol. 25, (2000), pp. 919-943 which is incorporated herein by reference]. Two potassium ions or a potassium atom may each provide an electron ionization or 10 transfer reaction that has a net enthalpy equal to an integer multiple of 27.2 eV. In the Mills-INP study, the spectral lines of atomic hydrogen were intense enough to be recorded on photographic films only when KI was present. EUV lines not assignable to potassium, iodine, or hydrogen shown in TABLE 3 15 were observed at 73.0, 132.6, 513.6, 677.8, 885.9, and 1032.9 Å. The lines could be assigned to transitions of atomic hydrogen to lower energy levels corresponding to lower energy hydrogen atoms called hydrino atoms and the emission from the excitation of the corresponding hydride ions formed from the hydrino 20 atoms.

TABLE 3. Observed emission data from hydrogen-KI plasmas produced by a hollow cathode discharge that can not be assigned to atomic or molecular hydrogen.

| Peak | INP Peak # | Observed Wave-length (Å) | Observed Energy (eV) | Peak Assignment | Predicted Energy (eV) | Predicted Wave-length (Å) |
|---------------|---------------|--------------------------|----------------------|---|-----------------------|---------------------------|
| 1 (inside) | # 24, # 30 | 73.0 | 169.9 | 1/4 → 1/6 H transition ^a | 176.8 | 70.2 |
| 3 | # 30 | 1032.9 | 12.0 | H-(1/4) ^{b,c} | 11.23 | 1104 |
| 19 | # 28 | 132.6 | 93.5 | 1/4 → 1/5 H transition ^d | 95.2 | 130.3 |
| 20 | # 28 | 885.9 | 14.0 | Inelastic H scattering of $H^*\left[\frac{a_H}{4}\right]$ ^e | 13.98 | 887.2 |
| 21 | # 30 | 513.6 | 25.15 | H-(1/6) ^c | 22.8 | 543 |
| 22 | # 30 | 677.8 | 18.30 | H-(1/5) ^c | 16.7 | 742 |

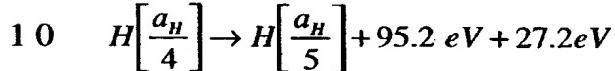
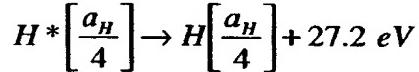
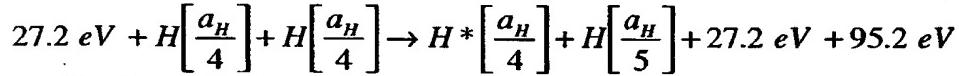
^a Transition induced by a resonance state excited in $H\left[\frac{a_H}{4}\right]$



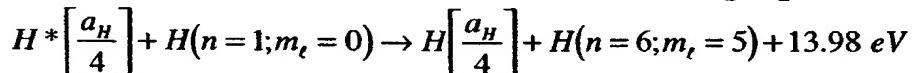
^b I⁺ has a peak at 1034.66 Å, [31] but none of the other iodine lines were detected including much stronger lines.

5 ^c The hydride ion emission is anticipated to be shift to shorter wavelengths due to its presence in a chemical compound.

^d Transition induced by a metastable state excited in $H\left[\frac{a_H}{4}\right]$



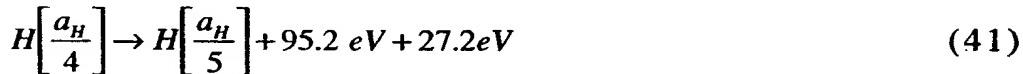
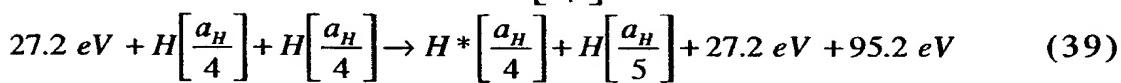
^e Hydrogen inelastic scattered peak of $H^*\left[\frac{a_H}{4}\right]$ deexcitation



The results support that potassium atoms reacted with
15 atomic hydrogen to form novel hydrogen energy states.

Potassium iodide present in the discharge of hydrogen served as a source of potassium metal which was observed to collect on the walls of the cell during operation. According to Eqs. (3-5), potassium metal reacts with atomic hydrogen present in the 5 discharge and forms the hydrino atom $H\left[\frac{a_H}{4}\right]$. The energy released was expected to undergo *internal conversion* to increase the brightness of the plasma discharge since this is the common mechanism of relaxation. This is consistent with observation.

10 The product, $H\left[\frac{a_H}{4}\right]$ may serve as a reactant to form $H\left[\frac{a_H}{5}\right]$ according to Eqs. (29-31). The transition of $H\left[\frac{a_H}{4}\right]$ to $H\left[\frac{a_H}{5}\right]$ induced by a resonance transfer of 27.21 eV, $m=1$ in Eq. (2) with a metastable state excited in $H\left[\frac{a_H}{4}\right]$ is represented by



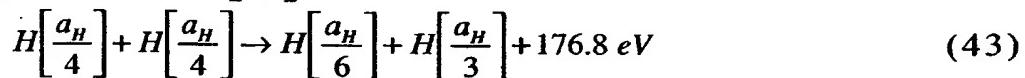
The energy emitted by a hydrino which has nonradiatively transferred $m \times 27.2 \text{ eV}$ of energy to a second hydrino may be emitted as a spectral line. Hydrinos may accept energy by a 20 nonradiative mechanism [Mills GUT]; thus, rather than suppressing the emission through internal conversion they do not interact with the emitted radiation. The predicted 95.2 eV (130.3 Å) photon (peak # 19) shown in FIGURE 29 of Mills-INP is a close match with the observed 132.6 Å line. In FIGURE 29 25 of Mills-INP, an additional peak (peak #20) was observed at 885.9 Å. It is proposed that peak #20 of Mills-INP arises from inelastic hydrogen scattering of the metastable state $H^*\left[\frac{a_H}{4}\right]$ formed by the resonant nonradiative energy transfer of 27.2 eV from a first $H\left[\frac{a_H}{4}\right]$ atom to a second as shown in Eq. (39). The 30 metastable state then nonradiatively transfers part of the

27.2 eV excitation energy to excite atomic hydrogen initially in the state $1s^2S_{1/2}$ to the state $6h^2H_{11/2}$. This leaves a 13.98 eV (887.2 Å) photon, peak 20. The initial and final states for all hydrogen species and emitted photons are determined by the selection rule for conservation of angular momentum where the 13.98 eV photon corresponds to $m_t = 0$ and the initial and final states for the hydrino atom reactants correspond to $m_t = 3$ and $m_t = -2$, respectively. In the case that the 95.2 eV (130.3 Å) photon (peak # 19) corresponds to $m_t = 0$ or ± 1 , then angular momentum is conserved. The excited state hydrogen may then emit hydrogen lines that are observed in FIGURE 29 of Mills-INP. Thus, the inelastic hydrogen scattering of the deexcitation of

$H^*\left[\frac{a_H}{4}\right]$ may be represented by

$$H^*\left[\frac{a_H}{4}\right](m_t = 3) + H(n = 1; m_t = 0) \rightarrow \\ H\left[\frac{a_H}{4}\right](m_t = -2) + H(n = 6; m_t = 5) + 13.98 \text{ eV}(m_t = 0) \quad (42)$$

The product of the catalysis of atomic hydrogen with potassium metal, $H\left[\frac{a_H}{4}\right]$, may serve as reactants to form $H\left[\frac{a_H}{3}\right]$ and $H\left[\frac{a_H}{6}\right]$ according to Eq. (32). The transition of $H\left[\frac{a_H}{4}\right]$ to $H\left[\frac{a_H}{6}\right]$ induced by a multipole resonance transfer of 54.4 eV, $m = 2$ in Eq. (2) and a transfer of 40.8 eV with a resonance state of $H\left[\frac{a_H}{3}\right]$ excited in $H\left[\frac{a_H}{4}\right]$ is represented by



The predicted 176.8 eV (70.2 Å) photon is a close match with the observed 73.0 Å line of Mills-INP.

The hydrinos are predicted to form hydrino hydride ions. A novel inorganic hydride compound *KHI* which comprises high binding energy hydride ions was synthesized by reaction of atomic hydrogen with potassium metal and potassium iodide [R. Mills, B. Dhandapani, N. Greenig, J. He, "Synthesis and Characterization of Potassium Iodo Hydride", Int. J. of Hydrogen Energy, Vol. 25, Issue 12, December, (2000), pp. 1185-1203].

The X-ray photoelectron spectroscopy (XPS) spectrum of *KHI* differed from that of *KI* by having additional features at 9.1 eV and 11.1 eV. The XPS peaks centered at 9.0 eV and 11.1 eV that do not correspond to any other primary element peaks may 5 correspond to the $H^-(n=1/4) E_b = 11.2 \text{ eV}$ hydride ion predicted by Mills [Mills GUT] (Eq. (36)) in two different chemical environments where E_b is the predicted vacuum binding energy. In this case, the reaction to form $H^-(n=1/4)$ is given by Eqs. (3- 10 5) and Eq. (38). Hydrino hydride ions $H^-(n=1/4)$, $H^-(n=1/5)$, and $H^-(n=1/6)$ corresponding to the corresponding hydrino atoms were anticipated. The predicted energy of emission due to these ions in the plasma discharge was anticipated to be higher than that given in TABLE 2 due to the formation of stable compounds such as *KHI* comprising these ions. Emission peaks 15 which could not be assigned to hydrogen, potassium, or iodine were observed at 1032.9 Å (12.0 eV), 677.8 Å (18.3 eV), and 513.6 Å (24.1 eV) [Mills-INP]. The binding energies of hydrino hydride ions $H^-(n=1/4)$, $H^-(n=1/5)$, and $H^-(n=1/6)$ corresponding to the corresponding hydrino atoms are 11.23 eV, 20 16.7 eV, and 22.81 eV. The emissions were 1 to 2 eV higher than predicted which may be due to the presence of these ions in compounds with chemical environments different from that of vacuum. The excitation was due to the plasma electron bombardment.

CLAIMS

1. A method of producing light, plasma, power, or compounds containing lower energy hydrogen comprising a reaction of lower energy atomic hydrogen whereby a catalyzed lower energy hydrogen atom serves as a reactant of a disproportionation reaction whereby it which accepts energy from an second catalyzed lower energy hydrogen atom to cause a further release of energy as the first atom undergoes a nonradiative electronic transition to a higher nonionized energy level while the second undergoes a transition to a lower energy level.
2. The method of claim 1 whereby lower-energy hydrogen atoms are generated by the catalysis of atomic hydrogen.
3. The method of claim 2 whereby the catalysis of atomic hydrogen comprises the reaction of atomic hydrogen with a catalyst that provides a net enthalpy of reaction of an integer multiple of 27.2 eV to form a hydrogen atom having a binding energy of $\text{Binding Energy} = \frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where p is an integer greater than 1, preferably from 2 to 200.
4. The method of claim 3 wherein the catalyst is selected from the group of Li, Be, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Kr, Rb, Sr, Nb, Mo, Pd, Sn, Te, Cs, Ce, Pr, Sm, Gd, Dy, Pb, Pt, He^+ , Na^+ , Rb^+ , Fe^{3+} , Mo^{2+} , Mo^{4+} , In^{3+} , He^+ , Ar^+ , Xe^+ , Ar^{2+} and H^+ , and Ne^+ and H^+ and K^+ .
5. The method of claim 1 further comprising a metastable excitation, resonance excitation, or ionization of a hydrino atom involving a nonradiative energy transfer between lower energy atoms of hydrogen of $m \times 27.2 \text{ eV}$ where m is an integer.
6. The method of claim 5 whereby the resonant transfer

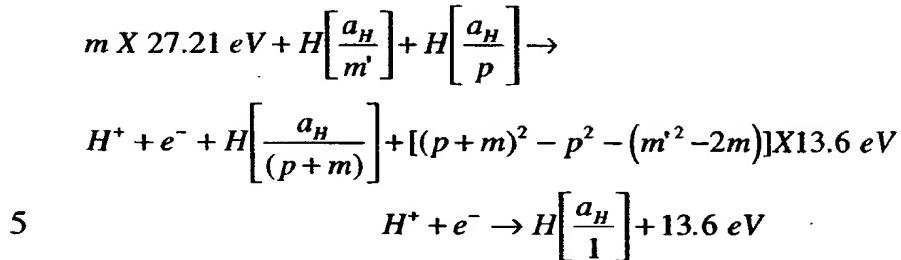
occurs in multiple stages.

7. The method of claim 1 comprising the transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced by a resonance transfer of $m \cdot 27.21 \text{ eV}$ with a metastable state excited in $H\left[\frac{a_H}{p'}\right]$ which is represented by
- $$m \cdot 27.2 \text{ eV} + H\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p}\right] \rightarrow H^*\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p+m}\right] + [(p+m)^2 - p^2] \times 13.6 \text{ eV}$$
- $$H^*\left[\frac{a_H}{p'}\right] \rightarrow H\left[\frac{a_H}{p'}\right] + m \cdot 27.2 \text{ eV}$$
- And, the overall reaction is
- $$H\left[\frac{a_H}{p}\right] \rightarrow H\left[\frac{a_H}{p+m}\right] + [(p+m)^2 - p^2] \times 13.6 \text{ eV}$$
- 10 where p , p' , and m are integers and the asterisk represents an excited metastable state.

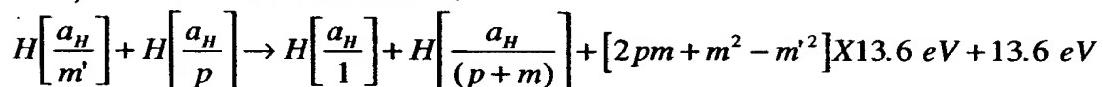
8. The method of claim 1 comprising the transition of $H\left[\frac{a_H}{p}\right]$ to $H\left[\frac{a_H}{p+m}\right]$ induced by a multipole resonance transfer of $m \cdot 27.21 \text{ eV}$ and a transfer of $[(p')^2 - (p'-m')^2] \times 13.6 \text{ eV} - m \cdot 27.2 \text{ eV}$ with a resonance state of $H\left[\frac{a_H}{p'-m'}\right]$ excited in $H\left[\frac{a_H}{p'}\right]$ which is represented by
- $$H\left[\frac{a_H}{p'}\right] + H\left[\frac{a_H}{p}\right] \rightarrow$$
- $$H\left[\frac{a_H}{p'-m'}\right] + H\left[\frac{a_H}{p+m}\right] + [(p+m)^2 - p^2] - (p'^2 - (p'-m')^2) \times 13.6 \text{ eV}$$
- 15 where p , p' , m , and m' are integers.

- 20 9. The method of claim 5 comprising a disproportionation reaction whereby the transition cascade for the p th cycle of the hydrogen-type atom, $H\left[\frac{a_H}{p}\right]$, with the hydrogen-type atom,

$H\left[\frac{a_H}{m'}\right]$, that is ionized as the source of a net enthalpy of reaction of $mX27.2\text{ eV}$ where m is an integer that causes the transition is represented by



And, the overall reaction is



10. The method of claim 1 wherein a lower energy hydrogen compound is produced comprising

(a) at least one neutral, positive, or negative increased binding energy hydrogen species having a binding energy

(i) greater than the binding energy of the corresponding ordinary hydrogen species, or

15 (ii) greater than the binding energy of any hydrogen species for which the corresponding ordinary hydrogen species is unstable or is not observed because the ordinary hydrogen species' binding energy is less than thermal energies at ambient conditions, or is negative; and

20 (b) at least one other element.

11. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the group consisting of H_n , H_n^- , and H_n^+ where n is a positive integer, with the proviso that n is greater than 1 when H has a positive charge.

12. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the

group consisting of (a) hydride ion having a binding energy that is greater than the binding of ordinary hydride ion (about 0.8 eV) for $p=2$ up to 23 in which the binding energy is represented

$$\text{by Binding Energy} = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right)$$

- 5 where p is an integer greater than one, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge; (b) hydrogen atom having a binding energy greater than about 13.6 eV; (c)
10 hydrogen molecule having a first binding energy greater than about 15.5 eV; and (d) molecular hydrogen ion having a binding energy greater than about 16.4 eV.

13. A method of claim 12 wherein the lower energy hydrogen
15 compound is produced which is characterized in that the increased binding energy hydrogen species is a hydride ion having a binding energy of about 3.0, 6.6, 11.2, 16.7, 22.8, 29.3, 36.1, 42.8, 49.4, 55.5, 61.0, 65.6, 69.2, 71.5, 72.4, 71.5, 68.8, 64.0, 56.8, 47.1, 34.6, 19.2, or 0.65 eV.

- 20 14. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is a hydride ion having the binding energy:

$$\text{Binding Energy} = \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right)$$

- where p is an integer greater than one, $s=1/2$, π is pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge.

15. A method of claim 10 wherein the lower energy hydrogen compound is produced which is characterized in that the increased binding energy hydrogen species is selected from the 5 group consisting of

(a) a hydrogen atom having a binding energy of about $\frac{13.6 \text{ eV}}{\left(\frac{1}{p}\right)^2}$ where p is an integer,

(b) an increased binding energy hydride ion (H^-) having a binding energy of about

$$10 \quad \frac{\hbar^2 \sqrt{s(s+1)}}{8\mu_e a_0^2 \left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^2} - \frac{\pi \mu_0 e^2 \hbar^2}{m_e^2 a_0^3} \left(1 + \frac{2^2}{\left[\frac{1 + \sqrt{s(s+1)}}{p} \right]^3} \right) \text{ where } s = 1/2, \pi \text{ is}$$

pi, \hbar is Planck's constant bar, μ_0 is the permeability of vacuum, m_e is the mass of the electron, μ_e is the reduced electron mass, a_0 is the Bohr radius, and e is the elementary charge;

(c) an increased binding energy hydrogen species $H_4^+(1/p)$;

15 (d) an increased binding energy hydrogen species trihydrino molecular ion, $H_3^+(1/p)$, having a binding energy of about $\frac{22.6}{\left(\frac{1}{p}\right)^2} \text{ eV}$ where p is an integer,

(e) an increased binding energy hydrogen molecule having a binding energy of about $\frac{15.5}{\left(\frac{1}{p}\right)^2} \text{ eV}$; and

20 (f) an increased binding energy hydrogen molecular ion with a binding energy of about $\frac{16.4}{\left(\frac{1}{p}\right)^2} \text{ eV}$.